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IBM Technical Disclosure Bulletins

Term: L12 and l4

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Search History

DATE: Thursday, June 20, 2002 Printable Copy Create Case

Set Name side by side	Query	Hit Count	Set Name result set
	DB=USPT,PGPB,JPAB,EPAB,DWPI; PLUR=YES; OP=ADJ		
L13	L12 and l4	27	L13
L12	organometallic complex	2084	L12
L11	L10 and l4	519	L11
L10	metal complex	32844	L10
L9	L8 and l4	2546	L9
L8	complex or metal complex	674847	L8
L7	L6 and l4	412	L7
L6	led or light emitting device	311421	L6
L5	l1 and L4	41	L5
L4	l2 same l3	7974	L4
L3	halogen or fluorine or chlorine or bromine or iodine or astatine or f or cl or br or i or at	6430752	L3
L2	pz or pyrazolyl or pyrazol-1-yl or pyrazol	19181	L2
L1	lanthanide	13440	L1

END OF SEARCH HISTORY

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* * * * * * * * * *   Welcome to STN International   * * * * * * * * * *

 NEWS  1          Web Page URLs for STN Seminar Schedule - N. America
 NEWS  2  Jan 25  BLAST(R) searching in REGISTRY available in STN on the Web
 NEWS  3  Jan 29  FSTA has been reloaded and moves to weekly updates
 NEWS  4  Feb 01  DKILIT now produced by FIZ Karlsruhe and has a new update
                  frequency
 NEWS  5  Feb 19  Access via Tymnet and SprintNet Eliminated Effective 3/31/02
 NEWS  6  Mar 08  Gene Names now available in BIOSIS
 NEWS  7  Mar 22  TOXLIT no longer available
 NEWS  8  Mar 22  TRCTHERMO no longer available
 NEWS  9  Mar 28  US Provisional Priorities searched with P in CA/CAplus
                  and USPATFULL
 NEWS 10  Mar 28  LIPINSKI/CALC added for property searching in REGISTRY
 NEWS 11  Apr 02  PAPERCHEM no longer available on STN.  Use PAPERCHEM2
instead.
 NEWS 12  Apr 08  "Ask CAS" for self-help around the clock
 NEWS 13  Apr 09  BEILSTEIN: Reload and Implementation of a New Subject Area
 NEWS 14  Apr 09  ZDB will be removed from STN
 NEWS 15  Apr 19  US Patent Applications available in IFICDB, IFIPAT, and
IFIUDB
 NEWS 16  Apr 22  Records from IP.com available in CAPLUS, HCAPLUS, and
ZCAPLUS
 NEWS 17  Apr 22  BIOSIS Gene Names now available in TOXCENTER
 NEWS 18  Apr 22  Federal Research in Progress (FEDRIP) now available
 NEWS 19  Jun 03  New e-mail delivery for search results now available
 NEWS 20  Jun 10  MEDLINE Reload
 NEWS 21  Jun 10  PCTFULL has been reloaded

 NEWS EXPRESS  February 1 CURRENT WINDOWS VERSION IS V6.0d,
               CURRENT MACINTOSH VERSION IS V6.0a(ENG) AND V6.0Ja(JP),
               AND CURRENT DISCOVER FILE IS DATED 05 FEBRUARY 2002
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FILE 'HOME' ENTERED AT 10:29:48 ON 20 JUN 2002

=> eg
EG IS NOT A RECOGNIZED COMMAND
The previous command name entered was not recognized by the system.
For a list of commands available to you in the current file, enter
"HELP COMMANDS" at an arrow prompt (=>).

=> fil reg
COST IN U.S. DOLLARS                                SINCE FILE      TOTAL
                                                         ENTRY    SESSION
FULL ESTIMATED COST                                       0.21       0.21

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DICTIONARY FILE UPDATES:   18 JUN 2002  HIGHEST RN 431976-32-8

TSCA INFORMATION NOW CURRENT THROUGH January 7, 2002

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Calculated physical property data is now available.  See HELP PROPERTIES
for more information.  See STNote 27, Searching Properties in the CAS
Registry File, for complete details:
http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf

=> ....Testing the current file.... screen

ENTER SCREEN EXPRESSION OR (END):end


=>
Uploading C:\STNEXP4\QUERIES\om1.str

L1        STRUCTURE UPLOADED

=> que L1

L2    QUE L1

=> d l2
L2 HAS NO ANSWERS
L1                STR

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY -  AVAILABLE VIA OFFLINE PRINT *

Structure attributes must be viewed using STN Express query preparation.
L2                QUE   L1


=> s l2
```

```
SAMPLE SEARCH INITIATED 10:30:19 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED -     35 TO ITERATE

100.0% PROCESSED      35 ITERATIONS                           16 ANSWERS
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS:  ONLINE   **COMPLETE**
                        BATCH    **COMPLETE**
PROJECTED ITERATIONS:           346 TO     1054
PROJECTED ANSWERS:               80 TO      560

L3            16 SEA SSS SAM L1

=> s l2 full
FULL SEARCH INITIATED 10:30:23 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED -    755 TO ITERATE

100.0% PROCESSED     755 ITERATIONS                          334 ANSWERS
SEARCH TIME: 00.00.02

L4           334 SEA SSS FUL L1

=> ....Testing the current file.... screen

ENTER SCREEN EXPRESSION OR (END):end


=>
Uploading C:\STNEXP4\QUERIES\om2.str

L5       STRUCTURE UPLOADED

=> que L5

L6   QUE L5

=> d l6
L6 HAS NO ANSWERS
L5                STR

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY -  AVAILABLE VIA OFFLINE PRINT *

Structure attributes must be viewed using STN Express query preparation.
L6                QUE  L5


=> s l6
SAMPLE SEARCH INITIATED 10:30:45 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED -    463 TO ITERATE

100.0% PROCESSED     463 ITERATIONS                            0 ANSWERS
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS:  ONLINE   **COMPLETE**
                        BATCH    **COMPLETE**
PROJECTED ITERATIONS:          7970 TO    10550
PROJECTED ANSWERS:                0 TO        0

L7             0 SEA SSS SAM L5
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=> s l6 full
FULL SEARCH INITIATED 10:30:53 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED -   9346 TO ITERATE

100.0% PROCESSED    9346 ITERATIONS                              6 ANSWERS
SEARCH TIME: 00.00.01

L8             6 SEA SSS FUL L5

=> fil caplus uspatfull biosis embase medline
COST IN U.S. DOLLARS                                  SINCE FILE     TOTAL
                                                           ENTRY   SESSION
FULL ESTIMATED COST                                       280.56    280.77

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FILE 'MEDLINE' ENTERED AT 10:31:04 ON 20 JUN 2002

=> d his

     (FILE 'HOME' ENTERED AT 10:29:48 ON 20 JUN 2002)

     FILE 'REGISTRY' ENTERED AT 10:29:53 ON 20 JUN 2002
L1                STRUCTURE UPLOADED
L2                QUE L1
L3             16 S L2
L4            334 S L2 FULL
L5                STRUCTURE UPLOADED
L6                QUE L5
L7              0 S L6
L8              6 S L6 FULL

     FILE 'CAPLUS, USPATFULL, BIOSIS, EMBASE, MEDLINE' ENTERED AT 10:31:04 ON
     20 JUN 2002

=> s l3
L9            20 L3

=> s l4
L10          812 L4

=> s l8
L11            7 L8

=> s l11 and halogen
L12            0 L11 AND HALOGEN

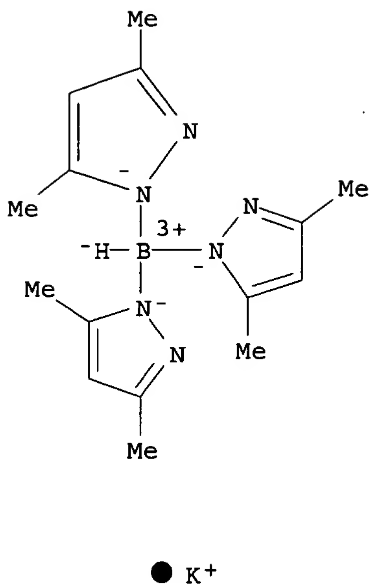
=> s l10 and halogen
```

```
L13          18 L10 AND HALOGEN

=> s l13 and metal
L14          16 L13 AND METAL

=> d ibib ab hitstr kwic 1-
YOU HAVE REQUESTED DATA FROM 16 ANSWERS - CONTINUE? Y/(N):y

L14  ANSWER 1 OF 16  CAPLUS  COPYRIGHT 2002 ACS
ACCESSION NUMBER:         1999:521608  CAPLUS
DOCUMENT NUMBER:          131:280539
TITLE:                    Synthesis and structural characterization of
                          face-sharing bioctahedral complexes containing
                          poly(pyrazolyl)borate ligands:
                          [HB(Me2Pz)3BH][X3Mo(.mu.-X)2(.mu.-H)MoTp*]  (X = Cl or
                          Br; Tp* = HB(Me2Pz)3; Pz = pyrazolyl)
AUTHOR(S):                Lee, C.-L.; Wu, Y.-Y.; Wu, C.-P.; Chen, J.-D.; Keng,
                          T.-C.; Wang, J.-C.
CORPORATE SOURCE:         Department of Chemistry, Chung-Yuan Christian
                          University, Chung-Li, Taiwan
SOURCE:                   Inorganica Chimica Acta (1999), 292(2), 182-188
                          CODEN: ICHAA3; ISSN: 0020-1693
PUBLISHER:                Elsevier Science S.A.
DOCUMENT TYPE:            Journal
LANGUAGE:                 English
AB   From a soln. prepd. by reaction of Mo2(O2CCH3)4 with KTp* (Tp* =
     hydridotris(3,5-dimethylpyrazolyl)borate, HB(Me2Pz)3), in glyme at room
     temp., followed by addn. of Me3SiCl and Me3SiBr to the red soln. in
     refluxing THF, brown [HB(Me2Pz)3BH][Cl3Mo(.mu.-Cl)2(.mu.-H)MoTp*] (1),
and
     [HB(Me2Pz)3BH][Br3Mo(.mu.-Br)2(.mu.-H)MoTp*] (2), resp., can be prepd.  A
     pink product [HB(Me2Pz)3BH][MoBr4(Me2PzH)2] (3), was also obtained during
     the prepn. of 2.  Their structures were detd. by x-ray crystallog.  The
     anions of complexes 1 and 2 consist of two octahedra sharing a common
     triangular face (face-sharing bioctahedral, FSBO), so that the Mo atoms
     are bridged by one H and two halogen atoms.  The unsym.
     metal centers are also chelated by tridentate Tp* ligands and
     coordinated by three halogen atoms.  In contrast to the sym.
     [Mo2X8H]3- (X = Cl, Br or I) ions whose Mo-Mo distances are hardly
     affected by the change in the size of the bridging halide atom, the
     variation of the Mo-Mo distance from 1 to 2 is .apprx.0.040 .ANG..  The
     formation of [HB(Me2Pz)3BH]+ and [MoBr4(Me2PzH)2]- shows the ready B-N
     bond cleavage of the Tp* ligand.
IT   17567-17-8, Potassium hydrotris(3,5-dimethylpyrazolyl)borate
     RL: RCT (Reactant); RACT (Reactant or reagent)
        (for prepn. of molybdenum .mu.-halo .mu.-hydrido
        hydridotris(pyrazolyl)borate face-sharing bioctahedral complexes)
RN   17567-17-8  CAPLUS
CN   Borate(1-), tris(3,5-dimethyl-1H-pyrazolato-.kappa.N1)hydro-, potassium,
     (T-4)- (9CI)   (CA INDEX NAME)
```



REFERENCE COUNT: 17 THERE ARE 17 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

AB From a soln. prepd. by reaction of Mo2(O2CCH3)4 with KTp* (Tp* = hydridotris(3,5-dimethylpyrazolyl)borate, HB(Me2Pz)3), in glyme at room temp., followed by addn. of Me3SiCl and Me3SiBr to the red soln. in refluxing THF, brown [HB(Me2Pz)3BH][Cl3Mo(.mu.-Cl)2(.mu.-H)MoTp*] (1), and [HB(Me2Pz)3BH][Br3Mo(.mu.-Br)2(.mu.-H)MoTp*] (2), resp., can be prepd. A pink product [HB(Me2Pz)3BH][MoBr4(Me2PzH)2] (3), was also obtained during the prepn. of 2. Their structures were detd. by x-ray crystallog. The anions of complexes 1 and 2 consist of two octahedra sharing a common triangular face (face-sharing bioctahedral, FSBO), so that the Mo atoms are bridged by one H and two **halogen** atoms. The unsym. **metal** centers are also chelated by tridentate Tp* ligands and coordinated by three **halogen** atoms. In contrast to the sym. [Mo2X8H]3- (X = Cl, Br or I) ions whose Mo-Mo distances are hardly affected by the change in the size of the bridging halide atom, the variation of the Mo-Mo distance from 1 to 2 is .apprx.0.040 .ANG.. The formation of [HB(Me2Pz)3BH]+ and [MoBr4(Me2PzH)2]- shows the ready B-N bond cleavage of the Tp* ligand.

IT 75-77-4, reactions 2857-97-8, Bromotrimethylsilane 14221-06-8, Dimolybdenum tetraacetate **17567-17-8**, Potassium hydrotris(3,5-dimethylpyrazolyl)borate
RL: RCT (Reactant); RACT (Reactant or reagent)
(for prepn. of molybdenum .mu.-halo .mu.-hydrido hydridotris(pyrazolyl)borate face-sharing bioctahedral complexes)

L14 ANSWER 2 OF 16 CAPLUS COPYRIGHT 2002 ACS
ACCESSION NUMBER: 1997:568727 CAPLUS
DOCUMENT NUMBER: 127:248532
TITLE: Transition **metal** compounds and their uses as polymerization catalysts for olefins
INVENTOR(S): Nakazawa, Hiroshi; Igai, Shigeru; Imaoka, Koji; Mitani, Nobuhiro
PATENT ASSIGNEE(S): Ube Industries, Ltd., Japan

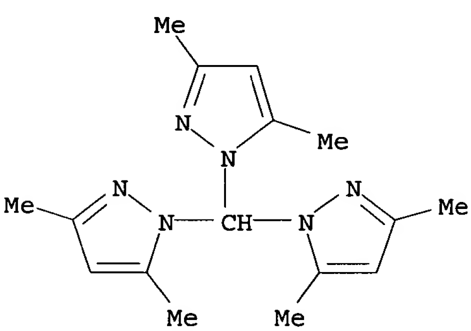
SOURCE: Jpn. Kokai Tokkyo Koho, 5 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 09220476	A2	19970826	JP 1996-28880	19960216

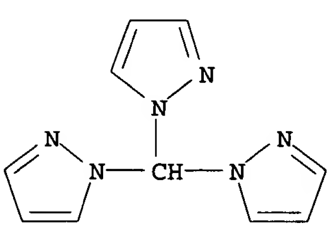
AB Title compds. RQPz3MYX2 (M = Group IV transition **metal**; PQPz3 = neutral trispyrazolyl ligands; Q = C, Si, Ge, Sn, Pb; R, X = H, **halogen**, C1-24 alkyl, aryl, cycloalkyl, amino, oxyhydrocarbyl; Y = O, S, Se, Te) are mixed with org. aluminumoxy compds. or Lewis acid compds. to give olefin polymn. catalysts. Thus, tris(pyrazolyl)methane and TiCl4-THF complex were reacted to give (HCPz3)Ti(O)Cl2. Ethylene was polymd. in the presence of 11.5 .mu.mol of the above compd. and 34.6 mmol methylaluminoxane in MePh at 40.degree. for 60 min to give polyethylene having wt. av. mol. wt. 249.000 and m.p. 134.3.degree..

IT **28791-97-1**, Tris(3,5-dimethylpyrazol-1-yl)methane
80510-03-8, Tris(pyrazol-1-yl)methane
RL: RCT (Reactant); RACT (Reactant or reagent)
(olefin polymn. catalysts contg. transition **metal** complex with trispyrazolyl-contg. ligands)

RN 28791-97-1 CAPLUS
CN 1H-Pyrazole, 1,1',1''-methylidynetris[3,5-dimethyl- (9CI) (CA INDEX NAME)



RN 80510-03-8 CAPLUS
CN 1H-Pyrazole, 1,1',1''-methylidynetris- (9CI) (CA INDEX NAME)



TI Transition **metal** compounds and their uses as polymerization catalysts for olefins

AB Title compds. RQPz3MYX2 (M = Group IV transition **metal**; PQPz3 = neutral trispyrazolyl ligands; Q = C, Si, Ge, Sn, Pb; R, X = H,

halogen, C1-24 alkyl, aryl, cycloalkyl, amino, oxyhydrocarbyl; Y = O, S, Se, Te) are mixed with org. aluminumoxy compds. or Lewis acid compds. to give olefin polymn. catalysts. Thus, tris(pyrazolyl)methane and TiCl4-THF complex were reacted to give (HCPz3)Ti(O)Cl2. Ethylene was polymd. in the presence of 11.5 .mu.mol of the above compd. and 34.6 mmol methylaluminoxane in MePh at 40.degree. for 60 min to give polyethylene having wt. av. mol. wt. 249.000 and m.p. 134.3.degree..

ST transition **metal** compd polymn catalyst olefin; trispyrazoylyl compd ligand titanium complex; ethylene polymn catalyst titanium trispyrazolylmehtane complex; polyethylene prepn polymn catalyst

IT Aluminoxanes
RL: CAT (Catalyst use); USES (Uses)
(Me, catalysts; olefin polymn. catalysts contg. transition **metal** complex with trispyrazolyl-contg. ligands)

IT Lewis acids
RL: CAT (Catalyst use); USES (Uses)
(catalysts; olefin polymn. catalysts contg. transition **metal** complex with trispyrazolyl-contg. ligands)

IT Group IVB elements
RL: CAT (Catalyst use); USES (Uses)
(complex; olefin polymn. catalysts contg. transition **metal** complex with trispyrazolyl-contg. ligands)

IT Polymerization catalysts
(olefin polymn. catalysts contg. transition **metal** complex with trispyrazolyl-contg. ligands)

IT Coordination compounds
RL: CAT (Catalyst use); IMF (Industrial manufacture); PREP (Preparation); USES (Uses)
(olefin polymn. catalysts contg. transition **metal** complex with trispyrazolyl-contg. ligands)

IT Alkenes, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(olefin polymn. catalysts contg. transition **metal** complex with trispyrazolyl-contg. ligands)

IT 9002-88-4P, Polyethylene
RL: IMF (Industrial manufacture); PREP (Preparation)
(olefin polymn. catalysts contg. transition **metal** complex with trispyrazolyl-contg. ligands)

IT 109-99-9D, THF, reaction products with titanium tetrachloride
7550-45-0D, Titanium chloride, reaction products with THF
28791-97-1, Tris(3,5-dimethylpyrazol-1-yl)methane
80510-03-8, Tris(pyrazol-1-yl)methane
RL: RCT (Reactant); RACT (Reactant or reagent)
(olefin polymn. catalysts contg. transition **metal** complex with trispyrazolyl-contg. ligands)

IT 195615-17-9P 195615-19-1P
RL: CAT (Catalyst use); IMF (Industrial manufacture); PREP (Preparation); USES (Uses)
(polymn. catalysts; olefin polymn. catalysts contg. transition **metal** complex with trispyrazolyl-contg. ligands)

L14 ANSWER 3 OF 16 CAPLUS COPYRIGHT 2002 ACS

ACCESSION NUMBER: 1997:308082 CAPLUS
DOCUMENT NUMBER: 126:287179
TITLE: **Metal** complexes as cysteine protease inhibitors
INVENTOR(S): Grinstaff, Mark W.; Gray, Henry B.; Meade, Thomas J.
PATENT ASSIGNEE(S): California Institute of Technology, USA
SOURCE: PCT Int. Appl., 64 pp.
CODEN: PIXXD2

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DOCUMENT TYPE:          Patent
LANGUAGE:               English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

     PATENT NO.       KIND  DATE          APPLICATION NO.  DATE
     ---------------  ----  --------      ---------------  --------
     WO 9711950        A1   19970403      WO 1996-US15527  19960927
         W:  AU, CA, IL, JP
         RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT,
SE
     CA 2232821        AA   19970403      CA 1996-2232821  19960927
     AU 9673767        A1   19970417      AU 1996-73767    19960927
     AU 728515         B2   20010111
     EP 862574         A1   19980909      EP 1996-936017   19960927
         R:  AT, BE, CH, DE, DK, FR, GB, IT, LI, NL, SE
     JP 11513381       T2   19991116      JP 1996-513680   19960927
PRIORITY APPLN. INFO.:                 US 1995-4451P    P 19950928
                                       WO 1996-US15527  W 19960927
OTHER SOURCE(S):        MARPAT 126:287179
```
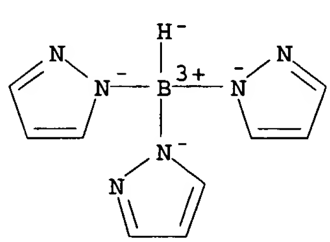

AB The invention relates to the prepn. of **metal** complexes (I) and related imine complexes used to bind proteins and enzymes, where M = Cu, Ag, Au, Ni, Pd or Pt; A = N or O; E = O, S, N or Se; D = C, B, P; X = a counterion or a neutral coordinating ligand; R1, R2, R3, R4, R5, R6, R7, R8 = H, **halogen**, alkyl, alkyl alc., alc., alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety; R1 may also be absent when A is oxygen, S, or Se; R2 may also be carbonyl oxygen, phosphonyl oxygen, or -OR5 when A is boron; R3 can also be -OR5 when A is boron or phosphorus, or absent when R2 is carbonyl oxygen; R6R7 = cycloalkyl, aryl; R8 may also be absent when E is oxygen, sulfur or selenium. Addnl., MLX (M = Cu, Ag, Au; L = hydrotris(pyrazolyl)borate deriv.), M(RR'CHSR'')X (M = Cu, Ag, Au, Ni, Pd, Pt), MLX2 (M = Cu, Ni, Pd, Pt; L = ethylenediamine deriv. or malonic acid deriv.). Thus, [CuLCl] was prepd. from salicylaldehyde, N-ethylethylenediamine and CuCl2 and was shown to nearly completely inhibit papain enzyme after 1 h (10 .mu.M enzyme, 25 .mu.M **metal** inhibitor).

IT **46755-84-4**, Hydrotris(pyrazolyl)borate(1-)
RL: RCT (Reactant)
(for prepn. of **metal** complexes as cysteine protease inhibitors)

RN 46755-84-4 CAPLUS

CN Borate(1-), hydrotris(1H-pyrazolato-.kappa.N1)-, (T-4)- (9CI) (CA INDEX NAME)



TI **Metal** complexes as cysteine protease inhibitors

AB The invention relates to the prepn. of **metal** complexes (I) and related imine complexes used to bind proteins and enzymes, where M = Cu, Ag, Au, Ni, Pd or Pt; A = N or O; E = O, S, N or Se; D = C, B, P; X = a

counterion or a neutral coordinating ligand; R1, R2, R3, R4, R5, R6, R7, R8 = H, **halogen**, alkyl, alkyl alc., alc., alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety; R1 may also be absent when A is oxygen, S, or Se; R2 may also be carbonyl oxygen, phosphonyl oxygen, or -OR5 when A is boron; R3 can also be -OR5 when A is boron or phosphorus, or absent when R2 is carbonyl oxygen; R6R7 = cycloalkyl, aryl;
R8 may also be absent when E is oxygen, sulfur or selenium. Addnl., MLX (M = Cu, Ag, Au; L = hydrotris(pyrazolyl)borate deriv.), M(RR'CHSR'')X (M = Cu, Ag, Au, Ni, Pd, Pt), MLX2 (M = Cu, Ni, Pd, Pt; L = ethylenediamine deriv. or malonic acid deriv.). Thus, [CuLCl] was prepd. from salicylaldehyde, N-ethylethylenediamine and CuCl2 and was shown to nearly completely inhibit papain enzyme after 1 h (10 .mu.M enzyme, 25 .mu.M **metal** inhibitor).

ST cysteine protease inhibitor Schiff complex prepn; transition **metal** Schiff prepn protease inhibitor; imine transition **metal** prepn protease inhibitor; thiol transition **metal** prepn protease inhibitor; enzyme inhibitor transition **metal** Schiff prepn; pyrazolylborato transition **metal** prepn protease inhibitor

IT Transition **metal** Schiff base complexes
Transition **metal** complexes
Transition **metal** imine complexes
Transition **metal** thiol complexes
RL: BAC (Biological activity or effector, except adverse); SPN (Synthetic preparation); THU (Therapeutic use); BIOL (Biological study); PREP (Preparation); USES (Uses)
(prepn. of transition **metal** complexes as protease inhibitors)

IT 56-40-6, Glycine, reactions 60-18-4, L-Tyrosine, reactions 90-02-8, reactions 99-96-7, reactions 107-15-3, 1,2-Ethanediamine, reactions 110-72-5, N-Ethylethylenediamine 123-90-0, Thiomorpholine 156-87-6, 3-Aminopropanol 556-33-2, Glycylglycylglycine 584-87-2, 3-Formyl-4-hydroxybenzoic acid 635-93-8, 5-Chlorosalicylaldehyde 1664-40-0, N-Phenylethylenediamine 6066-82-6, N-Hydroxysuccinimide 10025-99-7, Potassium tetrachloroplatinate 16903-35-8, Tetrachloroauric acid 17355-09-8 **46755-84-4**, Hydrotris(pyrazolyl)borate(1-)
RL: RCT (Reactant)
(for prepn. of **metal** complexes as cysteine protease inhibitors)

IT 94-93-9P, Salen 1952-38-1P 42164-12-5P 110881-33-9P 188907-02-0P 188907-03-1P 188907-04-2P 188907-05-3P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation)
(for prepn. of **metal** complexes as cysteine protease inhibitors)

IT 9001-73-4, Papain 37353-41-6, Cysteine protease
RL: BAC (Biological activity or effector, except adverse); BIOL (Biological study)
(prepn. of **metal** complexes as cysteine protease inhibitors)

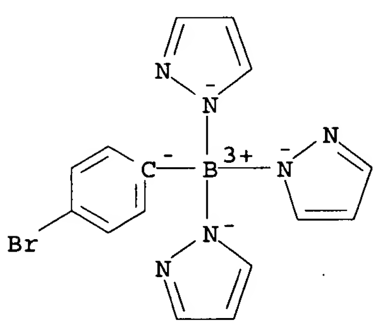
IT 7440-02-0DP, Nickel, complexes 7440-05-3DP, Palladium, complexes 7440-06-4DP, Platinum, complexes 7440-22-4DP, Silver, complexes 7440-50-8DP, Copper, complexes 7440-57-5DP, Gold, complexes 13987-24-1P 14167-15-8P 14167-20-5P 14242-80-9P 14729-94-3P 64811-69-4P 105096-21-7P 120771-64-4P 188906-96-9P 188906-97-0P 188906-98-1P 188906-99-2P 188907-00-8P 188907-01-9P 188907-06-4P
RL: BAC (Biological activity or effector, except adverse); SPN (Synthetic preparation); THU (Therapeutic use); BIOL (Biological study); PREP (Preparation); USES (Uses)
(prepn. of **metal** complexes as cysteine protease inhibitors)

L14 ANSWER 4 OF 16 CAPLUS
ACCESSION NUMBER: 1982:122988 CAPLUS

DOCUMENT NUMBER: 96:122988
TITLE: Covalently bound paramagnetic shift reagents. 1. A versatile lithium reagent derived from bis[(4-bromophenyl)tris(1-pyrazolyl)borato]cobalt(II)
AUTHOR(S): White, David L.; Faller, J. W.
CORPORATE SOURCE: Dep. Chem., Yale Univ., New Haven, CT, 06520, USA
SOURCE: J. Am. Chem. Soc. (1982), 104(6), 1548-52
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: English

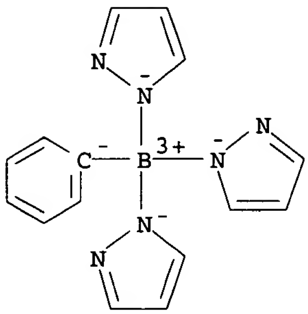
AB A versatile precursor for the attachment of covalently bound paramagnetic probes was prepd. Na (4-bromophenyl)tris(1-pyrazolyl)borate, 4-BrC6H4B(pz)3Na, was converted to the 4-lithio deriv. via **metal -halogen** exchange with BuLi in THF at -70.degree.. Deuteration of this Li reagent could be effected by treatment with D2O; carbonation, however, led to decompn. Conversion of [4-BrC6H4B(pz)3]2CoII to the corresponding 4-lithio compd. followed by deuteration, coupling with 1-iodobutane, or carbonation gave [4-RC6H4B(pz)3]2CoII (R = D, Bu, CO2H, resp.). The large isotropic shifts obsd. for protons on the Ph ring and its substituents can be predicted accurately using conventional expressions for the dipolar shift.

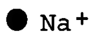
IT **80593-37-9P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. and lithium deriv. from)
RN 80593-37-9 CAPLUS
CN Borate(1-), (4-bromophenyl)tris(1H-pyrazolato-N1)-, sodium, (T-4)- (9CI) (CA INDEX NAME)



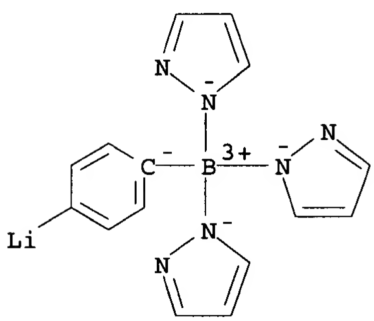
● Na+

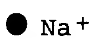
IT **80583-77-3P 80583-78-4P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)
RN 80583-77-3 CAPLUS
CN Borate(1-), phenyltris(1H-pyrazolato-N1)-, sodium, (T-4)- (9CI) (CA INDEX
NAME)





RN 80583-78-4 CAPLUS
CN Lithate(1-), .mu.-1,4-phenylene[tris(1H-pyrazolato-N1)borate]-, sodium (9CI) (CA INDEX NAME)





AB A versatile precursor for the attachment of covalently bound paramagnetic probes was prepd. Na (4-bromophenyl)tris(1-pyrazolyl)borate, 4-BrC6H4B(pz)3Na, was converted to the 4-lithio deriv. via **metal -halogen** exchange with BuLi in THF at -70.degree.. Deuteration of this Li reagent could be effected by treatment with D2O; carbonation, however, led to decompn. Conversion of [4-BrC6H4B(pz)3]2CoII to the corresponding 4-lithio compd. followed by deuteration, coupling with 1-iodobutane, or carbonation gave [4-RC6H4B(pz)3]2CoII (R = D, Bu, CO2H, resp.). The large isotropic shifts obsd. for protons on the Ph ring and its substituents can be predicted accurately using conventional expressions for the dipolar shift.

IT 80583-79-5P **80593-37-9P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. and lithium deriv. from)

IT **80583-77-3P** **80583-78-4P** 80583-80-8P 80583-81-9P 80583-82-0P 80583-83-1P 80593-38-0P
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)

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L14  ANSWER 5 OF 16  USPATFULL
ACCESSION NUMBER:        2002:63995  USPATFULL
TITLE:                   Reduced oxidation state transition metal
                         compounds useful as olefin polymerization catalysts
INVENTOR(S):             Matsunaga, Phillip T., Houston, TX, United States
                         Schiffino, Rinaldo S., Kingwood, TX, United States
PATENT ASSIGNEE(S):      Exxon Mobil Chemical Patents Inc., Houston, TX, United
                         States (U.S. corporation)

                              NUMBER        KIND    DATE
                         ---------------- ------ --------
PATENT INFORMATION:      US 6362294         B1   20020326
APPLICATION INFO.:       US 1997-989295          19971211  (8)
DOCUMENT TYPE:           Utility
FILE SEGMENT:            GRANTED
PRIMARY EXAMINER:        Wu, David W.
ASSISTANT EXAMINER:      Choi, Ling-Siu
LEGAL REPRESENTATIVE:    Muller, William G., Runyan, Charles E.
NUMBER OF CLAIMS:        32
EXEMPLARY CLAIM:         1
NUMBER OF DRAWINGS:      3 Drawing Figure(s); 1 Drawing Page(s)
LINE COUNT:              918
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
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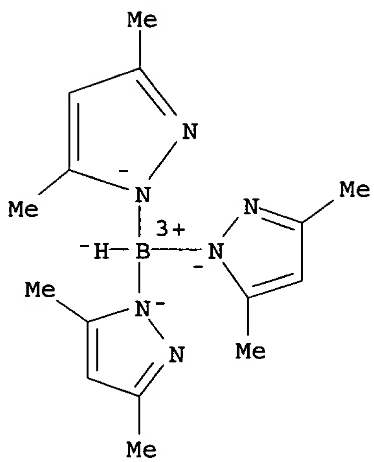
AB   This invention is directed to reduced oxidation state Group 4-6 **metal** compounds, preferably the first row metals in those groups, suitable for activation as polymerization catalysts and characterized by comprising a substituted hydrotris(pyrazolyl)borate ancillary ligand and a plurality of single or multidentate uninegative ligands, excluding cyclopentadienyl ligands. The invention includes a polymerization process characterized by comprising contacting one or more monomers polymerizable by coordination or insertion polymerization under suitable polymerization conditions with these catalyst compositions.

IT   **17567-17-8**
(reduced oxidn. state transition metal compds. useful as olefin polymn.
catalysts)

RN   17567-17-8 USPATFULL

CN   Borate(1-), tris(3,5-dimethyl-1H-pyrazolato-.kappa.N1)hydro-, potassium, (T-4)- (9CI) (CA INDEX NAME)



● K+

TI Reduced oxidation state transition **metal** compounds useful as olefin polymerization catalysts

AB This invention is directed to reduced oxidation state Group 4-6 **metal** compounds, preferably the first row metals in those groups, suitable for activation as polymerization catalysts and characterized by comprising a. . .

SUMM This invention relates to organometallic compounds comprising a Group 4-6 transition **metal** compound in which the **metal** is in a reduced oxidation state and which when activated by cocatalyst compounds, are suitable olefin polymerization catalysts.

SUMM . . . thermoplastic compositions of matter from olefins, such as polyethylene, polypropylene, and ethylene propylene rubber. Early pioneers utilized the early transition **metal** compounds, particularly those of the Group 4 metals, with such activators as aluminum alkyl compounds. Later developments extended this work to bulky ancillary ligand-containing (e.g., .eta.5-cyclopentadienyl) transition **metal** compounds ("metallocenes") with activators such as alkyl alumoxanes. Representative work addressing polymer molecular weight effects of substituted mono and bis. . .

SUMM Transition **metal** polymerization catalyst systems from Group 5-10 metals wherein the active transition **metal** center is in a high oxidation state and stabilized by low coordination number polyanionic ancillary ligand systems are described in. . . Example 1 illustrates tris(pyrazolyl)borato vanadium oxide dichloride, a d.sup.0 vanadium compound, and ethylene polymerization with it. Reduced Group 4-6 transition **metal** complexes useful as polymerization catalysts are described in WO96/13529. These complexes comprise a multidentate monoanionic ligand and two monoanionic ligands,. . .

SUMM . . . in the +4 or +5 oxidation states. With few exceptions, the use of tris(pyrazolyl)borate ("Tp") complexes as catalysts involves d.sup.0 **metal** centers, as noted. The only prior art exemplifying a non-d.sup.0 **metal** complex, WO 97/17379 in comparative example 12, shows such to have extremely low activity and to be essentially ineffective.

SUMM This invention is directed to reduced oxidation state Group 4-6 **metal** compounds, (those having d.sup.1-d.sup.3 electron

configurations) preferably the first row metals in those groups, suitable for activation as polymerization catalysts. . .

DETD The invention **metal** compounds described above can be generically represented by the following chemical formula:

DETD where Tp is a substituted tris(pyrazolyl)borate ligand; M is a Group 4-6 transition **metal**; X is independently **halogen**, alkoxide, aryloxide, amide, phosphide, hydride, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl; hydrocarbyl- or halocarbyl-substituted organometalloid, or two groups are joined and bound to the primary ligand or transition **metal** to form a ring structure, or one or more groups can contain a neutral donor group; L is a neutral donor group which stabilizes the complex; n is a number which is determined by counterbalancing the charge on the **metal** such that the **metal** remains in a reduced oxidation state and the overall charge on the precursor complex is neutral; p is a number. . .

DETD . . . for the L neutral donor groups include any neutral Lewis base compounds capable of donating an electron pair to the **metal** center. Non-limiting examples include diethylether, trimethylamine, tetrahydrofuran, dimethylaniline, aniline, trimethylphosphine, n-butylamine, and the like.

DETD The **metal** compounds according to the invention may be activated for insertion polymerization catalysis by known methods for either of Ziegler-Natta or metallocene transition **metal** compounds suitable for coordination polymerization. This activation is achieved for coordination polymerization by the inclusion of at least one reactive **metal**-ligand sigma bond ligand and at least one single vacant orbital adjacent (cis) to the sigma bound ligand, as is achieved. . . Ziegler organometallic cocatalysts and alumoxane compounds, and ionizing, anion precursor compounds that abstract one ligand so as to ionize the **metal** center into a cationic complex and provide a counter-balancing weakly or noncoordinating anion.

DETD The Ziegler cocatalyst will typically be an organometallic compound of a **metal** of Groups 1, 2, 12 or 13 of the Periodic table of elements. Preferred are organoaluminum compounds selected from the. . .

DETD . . . is independently a hydride or C.sub.1 to C.sub.10 hydrocarbyl radicals including aliphatic, alicyclic or aromatic hydrocarbon radicals, X' is a **halogen** and s is an integer from 1 to 3; and,

DETD Alkylalumoxanes and modified alkylalumoxanes are suitable as catalyst activators, particularly for the invention **metal** compounds comprising halide ligands. The alumoxane component useful as catalyst activator typically is an oligomeric aluminum compound represented by the. . .

DETD When the activator is an alumoxane, the preferred transition **metal** compound to activator molar ratio is from 1:2000 to 10:1, more preferably from about 1:500 to 10:1, even more preferably. . .

DETD The term "noncoordinating anion" is recognized to mean an anion which either does not coordinate to the **metal** cation or which is only weakly coordinated to it thereby remaining sufficiently labile to be displaced by a neutral Lewis. . .

DETD Descriptions of ionic catalysts, those comprising a transition **metal** cationic complex and a noncoordinating anion, suitable for coordination polymerization appear in the early work in U.S. Pat. Nos.

5,064,802,. . . wherein metallocenes are protonated by noncoordinating anion precursors such that an alkyl/hydride group is abstracted by protonation from a transition **metal** to make it both cationic and charge-balanced by the noncoordinating anion. Since the abstraction and insertion ligands of such metallocenes also may be ligands of the **metal** compounds of the invention, similar methods of preparation as active polymerization catalyst components may be followed.

DETD The use of ionizing ionic compounds not containing an active proton but capable of producing both an active **metal** cationic complex and a noncoordinating anion is also useful. See, EP-A-0 426 637, EP-A-0 573 403 and U.S. Pat. No.. . . cations of the ionizing ionic compounds, other than the Bronsted acids, include ferrocenium, silver, tropylium, triphenylcarbenium and triethylsilylium, or alkali **metal** or alkaline earth **metal** cations such as sodium, magnesium or lithium cations. A further class of noncoordinating anion precursors suitable in accordance with this invention are hydrated salts comprising the alkali **metal** or alkaline earth **metal** cations and a non-coordinating anion as described above. The hydrated salts can be prepared by reaction of the **metal** cation-noncoordinating anion salt with water, for example, by hydrolysis of the commercially available or readily synthesized LiB(pfp).sub.4 which yields [Li.xH.sub.2O]. . .

DETD Any **metal** or metalloid capable of forming a coordination complex which is resistant to degradation by water (or other Bronsted or Lewis. . .

DETD . . . the active polymerization catalysts of this invention uses ionizing anion pre-cursors which are initially neutral Lewis acids but form a **metal** cationic complex and the noncoordinating anion upon ionizing reaction with the invention compounds, for example tris(pentafluorophenyl)boron acts to abstract a hydrocarbyl, hydride or silyl ligand to yield an invention **metal** cationic complex and stabilizing noncoordinating anion, see EP-A-0 427 697 and EP-A-0 520 732 for illustration utilizing analogous Group 4. . .

DETD . . . protons or protonated Lewis bases (excluding water), or a reducible Lewis acid such as ferrocenium or silver cations, or alkaline **metal** or alkaline earth **metal** cations such as those of sodium, magnesium or lithium cations, the transition **metal** to activator molar ratio may be any ratio, but preferably from about 10:1 to 1:10, more preferably from about 5:1. . .

DETD . . . catalytic activity, particularly when ionizing anion pre-cursors activate the catalyst system. The polar impurities, or catalyst poisons include water, oxygen, **metal** impurities, etc. Preferably steps are taken before provision of such into the reaction vessel, for example by chemical treatment or. . .

DETD . . . methylalumoxane, isobutyl aluminumoxane, and n-octyl aluminum. Those scavenging compounds having bulky or C.sub.6-C.sub.20 linear hydrocarbyl substituents covalently bound to the **metal** or metalloid center being preferred to minimize adverse interaction with the active catalyst. Examples include triethylaluminum, but more preferably, bulky. . .

DETD . . . is that described U.S. Pat. No. 5,643,847, and WO 96/04319. A bulk, or slurry, process utilizing supported, invention Group 4-6 **metal** compounds activated with alumoxane co-catalysts can be utilized as application. Both inorganic oxide and polymeric supports may be utilized in. . .

DETD Advantageously, the ligand behavior in the coordination environment around the **metal** center permits the ready preparation of mixed polymer blends with a single **metal** compound according to the invention in a single polymerization reactor. One method of tailoring the properties of a polymer resin. . .

DETD . . . the invention contain components that can show lability. Variable temperature NMR studies can verify the lability of ligand components in **metal** complexes and neutral donor ligands, as exist in the catalysts of the invention, generally show the greatest degree of lability.. . .

DETD . . . same or different identity to the labile components or external acceptor species that can abstract the labile component from the **metal** center. Examples 9-11 below illustrate broad polydispersity polyethylene blends achieved with a single invention **metal** compound utilized at different temperatures of polymerization.

DETD The use of reduced **metal** centers is significant for the present invention because the presence of additional electrons on the **metal** center, relative to do complexes, may increase the lability of donor groups in the coordination sphere. Also, since six-coordinate, pseudooctahedral. . . the presence of additional neutral donor ligands. However, for non-d.sup.0 complexes in a +3 oxidation state, the charge on the **metal** can be balanced by one Tp ligand and 2 X ligands. This leaves one coordination site still available, and thus,. . .

CLM What is claimed is:

. . . reaction product of a cocatalyst and a catalyst precursor wherein the catalyst precursor comprises a reduced oxidation state Group 4-6 **metal** compound having a substituted tris(pyrazolyl)borate ligand and a plurality of single or multidentate uninegative ligands, excluding cyclopentadienyl ligands, and at. . .

2. The catalyst composition of claim 1 wherein the **metal** of said Group 4-6 **metal** compound is selected from the group consisting of Ti, V, and Cr.

3. The catalyst composition of claim 1 wherein the **metal** of said Group 4-6 **metal** compound is vanadium.

4. The catalyst composition of claim 1 wherein said Group 4-6 **metal** compound is represented by the formula: TpMX.sub.nL.sub.p where Tp is a substituted tris(pyrazolyl)borate ligand; M is a Group 4-6 transition **metal**; X is **halogen**, alkoxide, aryloxide, amide, phosphide, hydride, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl; hydrocarbyl- or halocarbyl-substituted organometalloid, or two groups are joined and bound to the primary ligand or transition **metal** to form a ring structure, or one or more groups can contain a neutral donor group; L is a neutral donor group which stabilizes the complex; n is a number which is determined by counterbalancing the charge on the **metal** such that the **metal** remains in a reduced oxidation state and the overall charge on said **metal** compound is neutral; p is a number from 1-3, as necessary to stabilize the compound.

7. The catalyst composition of claim 4 wherein said **metal** compound is reacted with an alkylalumoxane or an aluminum alkyl cocatalyst.

9. The catalyst composition of claim 4 wherein said **metal** compound is reacted with an ionizing noncoordination anion cocatalyst.

. . . of coordination polymerization and insertion polymerization under suitable polymerization conditions with a catalyst comprising a reduced oxidation state Group 4-6 **metal** compound having a substituted tris(pyrazolyl)borate ancillary ligand and a plurality of single or multidentate uninegative ligands, excluding cyclopentadienyl ligands, and. . .

11. The process of claim 10 wherein the **metal** of said Group 4-6 **metal** compound is selected from the group consisting of Ti, V, and Cr.

12. The process of claim 10 wherein the **metal** of said Group 4-6 **metal** compound is vanadium.

13. The process of claim 10 wherein said Group 4-6 **metal** compound is represented by the formula: TpMX.sub.nL.sub.p where Tp is a substituted tris(pyrazolyl)borate ligand; M is a Group 4-6 transition **metal**; X is **halogen**, alkoxide, aryloxide, amide, phosphide, hydride, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl; hydrocarbyl- or halocarbyl-substituted organometalloid, or two groups are joined and bound to the primary ligand or transition **metal** to form a ring structure, or one or more groups can contain a neutral donor group; L is a neutral donor group which stabilizes the complex; n is a number which is determined by counterbalancing the charge on the **metal** such that the **metal** remains in a reduced oxidation state and the overall charge on said **metal** compound is neutral; p is a number from 1-3, as necessary to stabilize the compound.

18. The process of claim 10 wherein said **metal** compound is reacted with an alkylalumoxane or an aluminum alkyl cocatalyst activator.

20. The process of claim 10 wherein said **metal** compound is reacted with an ionizing noncoordination anion cocatalyst.

. . . are prepared in situ in a single polymerization reactor with a single one of said reduced oxidation state Group 4-6 **metal** compounds.

. . . coordination polymerization and insertion polymerization under suitable polymerization conditions with an activated catalyst comprising a reduced oxidation state Group 4-6 **metal** compound having a substituted tris(pyrazolyl)borate ancillary ligand and a plurality of single or multidentate uninegative ligands, excluding cyclopentadienyl ligands, and. . .

32. The process of claim 31 wherein said Ziegler cocatalyst is an organometallic compound of a **metal** of Groups 1, 2, 12, or 13 of the Periodic Table of Elements.

IT 10170-68-0 **17567-17-8** 18039-90-2, Titanium trichloride tris(tetrahydrofuran) 19559-06-9
(reduced oxidn. state transition metal compds. useful as olefin polymn. catalysts)

L14 ANSWER 6 OF 16 USPATFULL

ACCESSION NUMBER: 2002:45247 USPATFULL

TITLE: Complexes having tris(pyrazolyl)borate ligands for forming films

INVENTOR(S): Uhlenbrock, Stefan, Boise, ID, United States
Vaartstra, Brian A., Nampa, ID, United States

PATENT ASSIGNEE(S): Micron Technology, Inc., Boise, ID, United States (U.S. corporation)

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 6352580	B1	20020305
APPLICATION INFO.:	US 2000-631498		20000803 (9)

RELATED APPLN. INFO.: Division of Ser. No. US 1998-141432, filed on 27 Aug 1998, now patented, Pat. No. US 6127192

DOCUMENT TYPE: Utility

FILE SEGMENT: GRANTED

PRIMARY EXAMINER: Klemanski, Helene

LEGAL REPRESENTATIVE: Mueting, Raasch & Gebhardt, P.A.

NUMBER OF CLAIMS: 27

EXEMPLARY CLAIM: 1

NUMBER OF DRAWINGS: 3 Drawing Figure(s); 3 Drawing Page(s)

LINE COUNT: 679

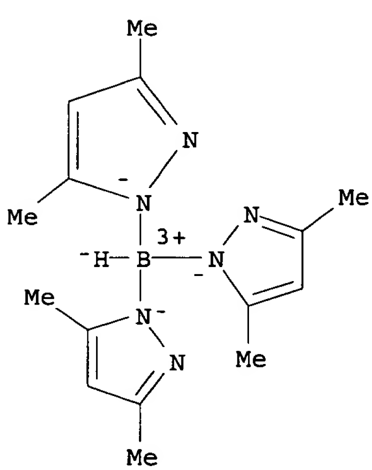
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Methods of forming a film on a substrate using chemical vapor deposition techniques and pyrazolyl complexes. The complexes and methods are particularly suitable for the preparation of semiconductor structures.

IT **155476-96-3 157044-88-7**
(complexes having tris(pyrazolyl) borate ligands for forming films by OMCVD in semiconductor device fabrication)

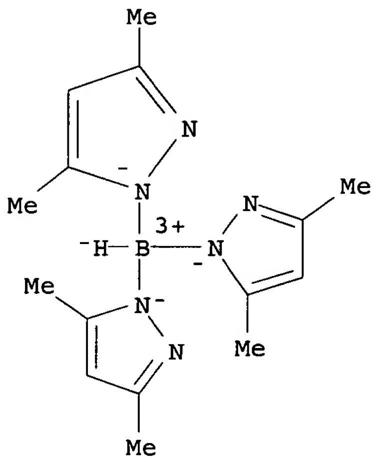
RN 155476-96-3 USPATFULL

CN Borate(1-), tris(3,5-dimethyl-1H-pyrazolato-.kappa.N1)hydro-, barium (2:1), (T-4)- (9CI) (CA INDEX NAME)



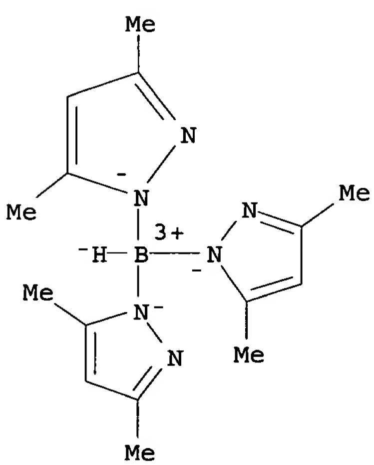
1/2 Ba^{2+}

RN   157044-88-7   USPATFULL
CN   Borate(1-), tris(3,5-dimethyl-1H-pyrazolato-.kappa.N1)hydro-, strontium (2:1), (T-4)- (9CI)   (CA INDEX NAME)



●1/2 Sr^{2+}

IT   **17567-17-8**
     (in prepn. of tris(pyrazolyl) borate complex)
RN   17567-17-8   USPATFULL
CN   Borate(1-), tris(3,5-dimethyl-1H-pyrazolato-.kappa.N1)hydro-, potassium, (T-4)- (9CI)   (CA INDEX NAME)



K^+

SUMM   This invention relates to methods of depositing films, such as **metal** oxide films, especially barium-strontium-titanate (BST)

films on substrates, particularly semiconductor device structures.

SUMM . . . random access memory (SRAM) devices, and now ferroelectric memory (FE RAM) devices. They consist of two conductors, such as parallel **metal** or polysilicon plates, which act as the electrodes (i.e., the storage node electrode and the cell plate capacitor electrode), insulated. . .

SUMM Suitable **metal** oxides are typically delivered to a substrate in the vapor phase; however, many oxides are difficult to deliver using vapor. . .

SUMM The present invention is directed to complexes and methods for forming **metal**-containing films on substrates, such as semiconductor substrates or substrate assemblies during the manufacture of semiconductor structures, particularly memory devices. The. . . having one or more tris(pyrazolyl)borate ligands (referred to herein as pyrazolyl complexes). Typically and preferably, the film is a dielectric **metal**-containing material. The **metal**-containing film can be an oxide, sulfide, selenide, telluride, nitride, or combination thereof, for example. Preferably, the film is a **metal** -containing oxide film. The film can be used as a dielectric layer in an integrated circuit structure, particularly in a memory. . .

SUMM . . . toward a substrate, such as a semiconductor substrate or substrate assembly, using a chemical vapor deposition technique to form a **metal**-containing film on a surface of the substrate, wherein the pyrazolyl complex includes one or more anionic tris(pyrazolyl)borate ligands of the. . .

SUMM . . . H or an organic group). Preferably, the pyrazolyl complex includes one or more ligands of Formula I attached to a **metal** selected from the group of the Group IIA (i.e., Group 2) metals, the Group IVB (i.e., Group 4) metals, the. . . or 4). For certain of the preferred embodiments, the precursor composition includes at least one pyrazolyl complex that includes a **metal** selected from the group of Zr, Hf, V, Nb, and Ta.

DETD . . . present invention provides a method of forming a film (preferably, an oxide film) using one or more pyrazolyl complexes (i.e., **metal** complexes containing one or more trispyrazolyl)borate ligands). Preferably, the pyrazolyl complexes are mononuclear (i.e., monomers) and display few intermolecular forces. . .

DETD . . . vaporizing a precursor composition, preferably a liquid precursor composition, that includes one or more pyrazolyl complexes. If more than one **metal** is desired in the resulting **metal** -containing film (i.e., if a **metal** alloy film is desired), the precursor composition can include more than one pyrazolyl complex. Alternatively, various percursor compositions can be. . .

DETD . . . gases that are generally unreactive with the pyrazolyl complexes described herein and do not interfere with the formation of a **metal**-containing film. Examples include nitrogen, helium, argon, and mixtures thereof. The reaction gas can be selected from a wide variety of. . .

DETD The designation "pyrazolyl complex" refers to a **metal** complex containing one or more anionic pyrazolyl ligands. Any of a variety of pyrazolyl ligands can be present in the. . . long as the complex can be used to form a film using chemical vaporization techniques. The pyrazolyl ligand stabilizes the **metal** complex and can be tailored to yield desired solubility and viscosity characteristics. Preferably, the anionic pyrazolyl ligand has the following. . .

DETD . . . or a halide, and preferably, the R.sup.4 group is H or an organic group. Such ligands can bond to a **metal** through one, two, or all three pyrazole groups.

DETD . . . aryloxy groups, and oxo groups. Preferably, the pyrazolyl complex includes one or more ligands of Formula I attached to a **metal** selected from the group of the Group IIA metals (i.e., Group 2 or alkaline earth metals), the Group IVB metals. . . y is 2 to 5 (preferably, 3 or 4). These complexes are monomers (i.e., mononuclear) in that they contain one **metal** per molecule.

DETD . . . the context of the present invention, the organic groups are those that do not interfere with the formation of a **metal** -containing film. Preferably, they are of a type and size that do not interfere with the formation of a **metal**-containing film using chemical vapor deposition techniques. The term "aliphatic group" means a saturated or unsaturated linear or branched hydrocarbon group.. . .

DETD . . . t-butyl, and the like, but also alkyl substituents bearing further substituents known in the art, such as hydroxy, alkoxy, alkylsulfonyl, **halogen** atoms, cyano, nitro, amino, carboxyl, etc. Thus, "alkyl group" includes ether groups, haloalkyls, nitroalkyls, carboxyalkyls, hydroxyalkyls, sulfoalkyls, etc. On the. . .

DETD In the pyrazolyl complexes of Formulas II-V, M refers to a **metal** of Groups IIA (alkaline earth metals), IVB (the titanium group), VA (Bi), and VB (the vanadium group). Preferred metals M. . .

DETD . . . pyrazolyl complexes of Formulas II-V of the present invention can be prepared by the above potassium pyrazolate with the appropriate **metal** halide (e.g., BaI.sub.2, SrI.sub.2, or Ti(OR).sub.2Cl.sub.2).

DETD . . . Formulas II-V. Such preferred precursor compositions can also include complexes of Groups IIA, IVB, VA, and VB metals or other **metal** or metalloid complexes that do not include the ligand of Formula I, as long as there is at least one. . .

DETD Methods of the present invention can be used to deposit a **metal** -containing film, preferably an oxide film, on a variety of substrates, such as a semiconductor wafer (e.g., silicon wafer, gallium arsenide.

. . that is not detrimental to the substrate, other layers thereon, etc. Preferably, however, solvents are not used; rather, the transition **metal** complexes are liquid and used neat. Methods of the present invention preferably utilize vapor deposition techniques, such as flash vaporization,. . .

DETD In this process, the precursor composition 40, which contains one or more pyrazolyl complexes (and/or other **metal** or metalloid complexes), is stored in liquid form (a neat liquid at room temperature or at an elevated temperature if. . .

DETD In this process, one or more solutions 60 of one or more pyrazolyl precursor complexes (and/or other **metal** or metalloid complexes), are stored in vessels 62. The solutions are transferred to a mixing manifold 64 using pumps 66.. . .

DETD . . . 1-3 are prepared by dissolving the solid compounds in THF to make 0.05M, 0.05M, and 0.1M solutions in the respective **metal**. The solutions are separately delivered to a vaporizer (COVA Technologies, Inc., Colorado Springs, Colo.) using syringe pumps. From here, the. . .

CLM What is claimed is:

. . . 1. A chemical vapor deposition precursor composition comprising two or more complexes comprising a Group IIA, IVB, VA, or VB **metal** and one or more anionic tris(pyrazolyl)borate ligands of the formula:

##STR3## wherein each R.sup.1, R.sup.2, R.sup.3, and R.sup.4 group is. . .

. . . from the group consisting of ML.sub.2, M(O)L.sub.2, M(OR.sup.5).sub.xL.sub.4-x, and M(OR.sup.5).sub.yL.sub.5-y; wherein: M is a Group IIA, IVB, VA, or VB **metal**; each R.sup.5 group is independently an organic group; x=2 to 4; y=2 to 5; L is an anionic ligand of. . .

. . . 3. A chemical vapor deposition precursor composition comprising one or more complexes comprising a Group IIA, IVB, VA, or VB **metal** , with the proviso that at least one complex includes a **metal** selected from the group consisting of Zr, Hf, V, Nb, and Ta, and one or more anionic tris(pyrazolyl)borate ligands of. . .

4. A **metal** complex of the formula M(O)L.sub.2, M(OR.sup.5).sub.xL.sub.4-x, and M(OR.sup.5).sub.yL.sub.5-y; wherein: M is a **metal** selected from the group consisting of Zr, Hf, V, Nb, and Ta; each R.sup.5 group is independently an organic group;. . .

5. The precursor composition of claim 1 wherein the **metal** is selected from the group of Ba, Sr, Ti, and mixtures thereof.

. . . M(O)L.sub.2, M(OR.sup.5).sub.xL.sub.4-x, and M(OR.sup.5).sub.yL.sub.5-y, wherein L is the anionic tris(pyrazolyl)borate ligand, M is a Group IIA, IVB, VA, or VB **metal**, R.sup.5 is an organic group, x=2to 4, and y=2 to 5.

. . . M(O)L.sub.2, M(OR.sup.5).sub.xL.sub.4-x, and M(OR.sup.5).sub.yL.sub.5-y, wherein L is the anionic tris(pyrazolyl)borate ligand, M is a Group IIA, IVB, VA, or VB **metal**, R.sup.5 is an organic group, x=2 to 4, and y=2 to 5.

9. The precursor composition of claim 1 further comprising one or more **metal** complexes that do not contain the anionic tris(pyrazolyl)borate ligand.

10. The precursor composition of claim 2 further comprising one or more **metal** complexes that do not contain the anionic tris(pyrazolyl)borate ligand.

11. The precursor composition of claim 3 further comprising one or more **metal** complexes that do not contain the anionic tris(pyrazolyl)borate ligand.

15. The **metal** complex of claim 4 wherein each R.sup.1, R.sup.2, R.sup.3, and R.sup.4 group is independently H or a (C.sub.1-C.sub.3,)organic group.

19. The **metal** complex of claim 4 wherein each R.sup.1, R.sup.2, R.sup.3, and R.sup.4 group is independently H or a (C.sub.1-C.sub.8)organic group.

23. The **metal** complex of claim 4 wherein R.sup.1 and R.sup.3 are methyl, and R.sup.2 and R.sup.4 are hydrogen.

27. The **metal** complex of claim 4 wherein each of R.sup.1 to R.sup.4 is hydrogen.

IT **155476-96-3** **157044-88-7** 157072-65-6 158444-73-6
(complexes having tris(pyrazolyl) borate ligands for forming films by

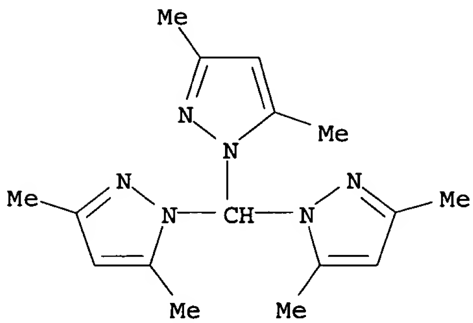
OMCVD in semiconductor device fabrication)
IT **17567-17-8**
(in prepn. of tris(pyrazolyl) borate complex)

L14 ANSWER 7 OF 16 USPATFULL
ACCESSION NUMBER: 2002:5967 USPATFULL
TITLE: Catalyst for trimerization of ethylene and process for trimerizing ethylene using the catalyst
INVENTOR(S): Mimura, Hideyuki, Shinnanyo, JAPAN
Oguri, Motohiro, Yokkaichi, JAPAN
Yamamoto, Toshihide, Yokkaichi, JAPAN
Murakita, Hideyuki, Yokkaichi, JAPAN
Okada, Hisanori, Yokkaichi, JAPAN
Yoshida, Toru, Kuwana, JAPAN
PATENT ASSIGNEE(S): Tosoh Corporation, Shinnanyo, JAPAN (non-U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 6337297	B1	20020108	
APPLICATION INFO.:	US 1999-457522		19991209	(9)

	NUMBER	DATE
PRIORITY INFORMATION:	JP 1998-351134	19981012
	JP 1998-352540	19981112

DOCUMENT TYPE: Utility
FILE SEGMENT: GRANTED
PRIMARY EXAMINER: Bell, Mark L.
ASSISTANT EXAMINER: Pasteczyk, J.
LEGAL REPRESENTATIVE: Oblon, Spivak, McClelland, Maier & Neustadt, P.C.
NUMBER OF CLAIMS: 13
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 0 Drawing Figure(s); 0 Drawing Page(s)
LINE COUNT: 1424
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
AB A catalyst for trimerization of ethylene is disclosed which comprises (a) a chromium complex having a neutral multidentate ligand having a tripod structure, represented by the formula, ACrJ.sub.nQ.sub.3-n wherein A is a neutral multidentate ligand having a tripod structure, J is a carbonyl ligand or **halogen**, n is an integer of 0-3, and Q is at least one member selected from hydrogen, a C.sub.1-C.sub.10 hydrocarbon group, a C.sub.1-C.sub.10 carboxylate group, a C.sub.3-C.sub.10 diketonato group, an amide group, an imide group, an C.sub.1-C.sub.10 alkoxide group, a C.sub.1-C.sub.10 thioalkoxide group, an C.sub.6-C.sub.15 arene ligand, an C.sub.2-C.sub.10 alkene ligand, an C.sub.2-C.sub.15 alkyne ligand, an amine ligand, an imine ligand, an isonitrile ligand, a phosphine ligand, a phosphine oxide ligand, a phosphite ligand, an ether ligand, a sulfide ligand, a sulfone ligand and a sulfoxide ligand, and (b) a **metal** alkyl compound. The catalyst optionally further comprises (c) at least one compound selected from aromatic tertiary amine compounds, except for an imine, and nitrogen-containing heterocyclic compounds, and (d) a radical anion compound.
IT **28791-97-1**, Tris(3,5-dimethyl-1-pyrazolyl)methane
(in prepn. of catalyst; prepn. of hexene by trimerization of ethylene)
RN 28791-97-1 USPATFULL
CN 1H-Pyrazole, 1,1',1''-methylidynetris[3,5-dimethyl- (9CI) (CA INDEX NAME)



AB . . . the formula, ACrJ.sub.nQ.sub.3-n wherein A is a neutral multidentate ligand having a tripod structure, J is a carbonyl ligand or **halogen**, n is an integer of 0-3, and Q is at least one member selected from hydrogen, a C.sub.1-C.sub.10 hydrocarbon group,. . . ligand, a phosphite ligand, an ether ligand, a sulfide ligand, a sulfone ligand and a sulfoxide ligand, and (b) a **metal** alkyl compound. The catalyst optionally further comprises (c) at least one compound selected from aromatic tertiary amine compounds, except for. . .

SUMM . . . Patent Publication No. (hereinafter abbreviated to "JP-A") S62-265237. A catalyst system comprising a chromium compound, a pyrrole-containing compound, an alkyl **metal** compound and a halide is described in JP-A H6-239920. A catalyst system comprising a chromium compound, an alkyl **metal** compound, and an acid amide or imide compound is described in JP-A HB-59732. A catalyst comprising (i) a complex of. . .

SUMM wherein A is a neutral multidentate ligand having a tripod structure, J is a carbonyl ligand or a **halogen** atom, n is an integer of 0 to 3, and Q is at least one member selected from the group. . .

SUMM (b) a **metal** alkyl compound.

SUMM The **halogen** atom J in formula (1) is not particularly limited, and includes, for example, fluorine, chlorine, bromine and iodine atoms.

SUMM The process for synthesizing the chromium **halogen** complex and other chromium complexes, which have a neutral multidentate ligand having a tripod structure, is not particularly limited. For example, the chromium **halogen** complex can be synthesized from a neutral multidentate ligand having a tripod structure and a chromium compound by known complex. . .

SUMM The chromium compounds used as a raw material for the synthesis of the chromium **halogen** complex and other chromium complexes are not particularly limited, and include, for example, chromium halides such as chromium chloride(III), chromium. . .

SUMM The concentration of chromium **metal** in a reaction solution for synthesis of the chromium complex is not particularly limited. The solvent used for the chromium. . .

SUMM . . . employed wherein the chromium complex having a neutral multidentate ligand having a tripod structure is synthesized by allowing a chromium **halogen** complex having a neutral multidentate

ligand having a tripod structure to react with a **metal** alkylamide, a **metal** alkoxide or a **metal** thioalkoxide in a solvent.

SUMM The chromium **halogen** complex having a neutral multidentate ligand having a tripod structure used is not particularly limited, and includes, for example, 1,1,1-tris(methoxymethyl)ethanechromium. . .

SUMM The **metal** alkylamide, **metal** alkoxide and **metal** thioalkoxide also are not particularly limited, and include, for example, lithium dimethylamide, lithium diethylamide, lithium diisopropylamide, lithium bis(trimethylsilyl)amide, sodium bis(trimethylsilyl)amide,. . .

SUMM . . . that the neutral multidentate ligand occupies the three coordinate sites to form an isomer of six-coordinate octahedral complex (Kagaku-sensho: Organic **Metal** Chemistry, Fundamental and Application, p143, published by Shoukabou, Japan). That is, the three coordinate sites occupied by the multidentate ligand. . .

SUMM The catalyst of the invention comprises a **metal** alkyl compound as another indispensable ingredient, in addition to the chromium complex of formula (1) having a neutral multidentate ligand having a tripod structure. The alkyl **metal** compound is not particularly limited, but those which are represented by the following formula (4) are preferable:

SUMM . . . an alkoxide group having 1 to 10 carbon atoms, an aryl group having 6 to 10 carbon atoms or a **halogen** atom.

SUMM . . . (4), there can be mentioned alkoxide groups such as methoxide, ethoxide, butoxide and phenoxide, aryl groups such as phenyl, and **halogen** atoms such as fluorine, chlorine, bromine and iodine.

SUMM In formula (4), when E is aluminum, each of p and q is 1.5, the **metal** alkyl compound is represented by the formula AlR.sub.1.5X.sub.1.5. Theoretically this compound does not exist, but, it is popularly called as a sesqui-compound of Al.sub.2R.sub.3X.sub.3 and can be used as the alkyl **metal** compound in the present invention.

SUMM As specific examples of the alkyl **metal** compound, there can be mentioned methyllithium, ethyllithium, propyllithium, n-butyllithium, s-butyllithium, t-butyllithium, diethylmagnesium, ethylbutylmagnesium, ethylchloromagnesium, ethylbromomagnesium, dimethylzinc, diethylzinc, dibutylzinc, trimethylborane, triethylborane,. . .

SUMM . . . aluminum compounds are preferable in view of commercial availability and catalytic activity. Triethylaluminum and triisobutylaluminum are especially preferable. These alkyl **metal** compounds may be used either alone or in combination.

SUMM . . . table, and two adjacent substituents thereof may form a ring together with the carbon atoms bonded thereto; M.sup.2 is a **metal** selected from the group consisting of alkali metals and alkaline earth metals and r is an integer of 1 when M.sup.2 is an alkali **metal** or an integer of 2 when M.sup.2 is an alkaline earth **metal**.

SUMM The **metal** M.sup.2 in formula (5) includes, for example, alkali metals such as lithium, sodium and potassium, and alkaline earth metals such. . .

SUMM . . . comprising (a) a chromium complex of formula (1) having a neutral multidentate ligand having a tripod structure, (b) an alkyl **metal** compound, (c) an optional compound selected from aromatic tertiary amine compounds, except for an imine, and nitrogen-containing heterocyclic compounds, and. . .

SUMM . . . light source, there can be mentioned a heavy hydrogen lamp, a xenon lamp, a tungsten lamp, an incandescent lamp, a **halogen**

lamp, a low pressure mercury lamp, a hollow cathode lamp, a **metal** vapor discharge tube, a **metal** halide lamp, high-pressure sodium lamp, a thallium lamp, a mercury-thallium lamp, a mercury-lead lamp, an H-type discharge tube, a xenon-mercury. . .

DETD . . . 2 3 4 5 6

Catalyst:
Cr complex A A A A A A
(.mu.mol) 16.0 16.0 8.0 4.0 1.0 4.0
Alkyl **metal** compound i-Bu.sub.3Al i-Bu.sub.3Al i-Bu.sub.3Al
i-Bu.sub.3Al i-Bu.sub.3Al i-Bu.sub.3Al
(.mu.mol) 240 240 240 240 240 480
Solvent Toluene CyHe Toluene Toluene Toluene Toluene
Reaction. . .

DETD . . . 9 1 2 3

Catalyst:
Cr complex A A B C D E
(.mu.mol) 4.0 4.0 16.0 16.0 16.0 16.0
Alkyl **metal** compound Et.sub.3Al Hex.sub.3Al i-Bu.sub.3Al
i-Bu.sub.3Al i-Bu.sub.3Al i-Bu.sub.3Al
(.mu.mol) 480 480 240 240 240 240
Solvent Toluene Toluene CyHe Toluene CyHe CyHe
Reaction. . .

DETD
TABLE 3

Example 10

Catalyst:
Cr complex G
(.mu.mol) 16.0
Alkyl **metal** compound i-Bu.sub.3Al
(.mu.mol) 240
Solvent Toluene
Reaction conditions:
Temperature (.degree. C.) 80
Pressure (kg/cm.sup.2) 5
Time (min) 30
Results:
Catalytic. . .

DETD . . . 12 13 14 15 16

Catalyst:
Cr complex A A A A A A
(.mu.mol) 4.0 4.0 4.0 4.0 4.0 4.0
Alkyl **metal** compound i-Bu.sub.3Al i-Bu.sub.3Al i-Bu.sub.3Al
i-Bu.sub.3Al i-Bu.sub.3Al i-Bu.sub.3Al
(.mu.mol) 480 480 480 480 480 480
Tertery aromatic amine PhNMe.sub.2 PhNMe.sub.2 PhNMe.sub.2 PhN(Pr-n).sub.2.
.
.

DETD
TABLE 5

Comparative Example 4 5 6

Catalyst:

Cr complex A A A
(.mu.mol) 4.0 4.0 4.0
Alkyl **metal** compound i-Bu.sub.3Al i-Bu.sub.3Al i-Bu.sub.3Al
(.mu.mol) 480 480 480
Tertiary aromatic amine -- C.sub.18H.sub.37NME.sub.2
(C.sub.12H.sub.25).sub.2NH
(.mu.mol) -- 40 40
Solvent Toluene Toluene Toluene
Reaction conditions:
Temperature (.degree.. . .
DETD
TABLE 6

Example 17 18

Catalyst:
Cr complex F F
(.mu.mol) 16.0 16.0
Alkyl **metal** compound i-Bu.sub.3Al i-Bu.sub.3Al
(.mu.mol) 240 240
n-BuLi
80
Solvent Toluene Toluene
Reaction conditions:
Temperature (.degree. C.) 80 80
Pressure (kg/cm.sup.2). . .
DETD
TABLE 7

Example 19 20

Catalyst:
Cr complex F F
(.mu.mol) 4.0 4.0
Alkyl **metal** compound i-Bu.sub.3Al i-Bu.sub.3Al
(.mu.mol) 960 590
Radical anion Na-na Na-na
(.mu.mol) 12 12
Solvent Toluene Toluene
Reaction conditions:
Temperature (.degree.. . .
DETD
TABLE 8

Example 21

Catalyst:
Cr complex G
(.mu.mol) 4.0
Alkyl **metal** compound i-Bu.sub.3Al
(.mu.mol) 960
Solvent Toluene
Reaction conditions:
Temperature (.degree. C.) 80
Pressure (kg/cm.sup.2) 5
Time (min) 30
Results:
Catalytic. . .
CLM What is claimed is:
. . . ACrJ.sub.nQ.sub.3-n (1) wherein A is a neutral multidentate ligand

having a tripod structure, J is a carbonyl ligand or a **halogen** atom, n is an integer of 0 to 3, and Q is at least one member selected from the group. . .

. . . an alkoxide group having 1 to 10 carbon atoms, an aryl group having 6
to 10 carbon atoms or a **halogen** atom.

. . . table, and two adjacent substituents thereof may form a ring together
with the carbon atoms bonded thereto; M.sup.2 is a **metal** selected from the group consisting of an alkali **metal** and an alkaline earth **metal**, and r is an integer of 1 when M.sup.2 is an alkali **metal** or an integer of 2 when M.sup.2 is an alkaline earth **metal**.

. . . an alkoxide group having 1 to 10 carbon atoms, an aryl group having 6
to 10 carbon atoms or a **halogen** atom.

. . . an alkoxide group having 1 to 10 carbon atoms, an aryl group having 6
to 10 carbon atoms or a **halogen** atom.

. . . ACrJ.sub.nQ.sub.3-n (1) wherein A is a neutral multidentate ligand having a tripod structure, J is a carbonyl ligand or a **halogen** atom, n is an integer of 0 to 3, and Q is at least one member selected from the group. . .

IT 13007-92-6, Chromium hexacarbonyl 22031-12-5, 1,1,1-Tris(diphenylphosphinomethyl)ethane **28791-97-1**, Tris(3,5-dimethyl-1-pyrazolyl)methane
(in prepn. of catalyst; prepn. of hexene by trimerization of ethylene)

L14 ANSWER 8 OF 16 USPATFULL

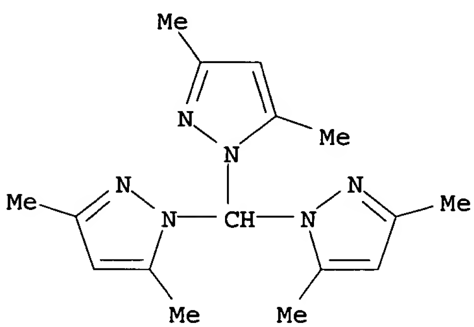
ACCESSION NUMBER: 2000:138249 USPATFULL
TITLE: Methods of forming a film on a substrate using complexes having tris(pyrazolyl) methanate ligands
INVENTOR(S): Uhlenbrock, Stefan, Boise, ID, United States
Vaartstra, Brian A., Nampa, ID, United States
PATENT ASSIGNEE(S): Micron Technology, Inc., Boise, ID, United States (U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 6133161		20001017	
APPLICATION INFO.:	US 1998-140914		19980827	(9)

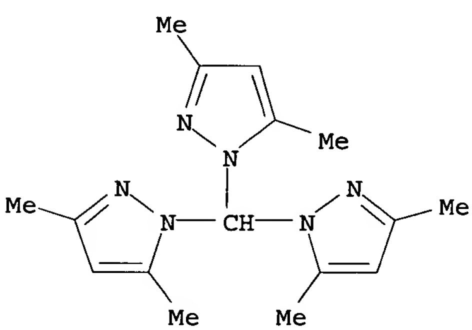
DOCUMENT TYPE: Utility
FILE SEGMENT: Granted
PRIMARY EXAMINER: Bowers, Charles
ASSISTANT EXAMINER: Thompson, Craig
LEGAL REPRESENTATIVE: Mueting, Raasch & Gebhardt, P.A.
NUMBER OF CLAIMS: 28
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 3 Drawing Figure(s); 3 Drawing Page(s)
LINE COUNT: 753
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Methods of forming a film on a substrate using chemical vapor deposition techniques and pyrazolyl complexes. The complexes and methods are particularly suitable for the preparation of semiconductor structures.

IT **28791-97-1 28791-97-1D**, metal complexes
(prepn. and reactions of lithium tris(dimethylpyrazolyl)methanate in prepn. of ligands for OMCVD)
RN 28791-97-1 USPATFULL
CN 1H-Pyrazole, 1,1',1''-methylidynetris[3,5-dimethyl- (9CI) (CA INDEX NAME)



RN 28791-97-1 USPATFULL
CN 1H-Pyrazole, 1,1',1''-methylidynetris[3,5-dimethyl- (9CI) (CA INDEX NAME)



SUMM This invention relates to methods of depositing films, such as **metal** oxide films, especially barium-strontium-titanate (BST) films on substrates, particularly semiconductor device structures.

SUMM . . . random access memory (SRAM) devices, and now ferroelectric memory (FE RAM) devices. They consist of two conductors, such as parallel **metal** or polysilicon plates, which act as the electrodes (i.e., the storage node electrode and the cell plate capacitor electrode), insulated. . .

SUMM Suitable **metal** oxides are typically delivered to a substrate in the vapor phase; however, many oxides are difficult to deliver using vapor. . .

SUMM The present invention is directed to complexes and methods for forming **metal**-containing films on substrates, such as semiconductor substrates or substrate assemblies during the manufacture of semiconductor structures, particularly memory devices. The. . . having one or more tris(pyrazolyl)methanate ligands (referred to herein as pyrazolyl complexes). Typically and preferably, the film is a dielectric **metal**-containing material. The **metal** -containing film can be an oxide, sulfide, selenide, telluride, nitride, or combination thereof. Preferably, the film is a **metal**

-containing oxide film. The film can be used as a dielectric layer in an integrated circuit structure, particularly in a memory. . .

SUMM . . . toward a substrate, such as a semiconductor substrate or substrate assembly, using a chemical vapor deposition technique to form a **metal**-containing film on a surface of the substrate, wherein the pyrazolyl complex includes one or more anionic tris(pyrazolyl)methanate ligands of the. . . organic group, or a halide. Preferably, the pyrazolyl complex includes one or more ligands of Formula I attached to a **metal** selected from the group of the Group IIA (i.e., Group 2) metals, the Group IVB (i.e., Group 4) metals, the. . .

DETD . . . present invention provides a method of forming a film (preferably, an oxide film) using one or more pyrazolyl complexes (i.e., **metal** complexes containing one or more tris(pyrazolyl)methanate ligands). Preferably, the pyrazolyl complexes are mononuclear (i.e., monomers) and display few intermolecular forces. . .

DETD . . . vaporizing a precursor composition, preferably a liquid precursor composition, that includes one or more pyrazolyl complexes. If more than one **metal** is desired in the resulting **metal** -containing film (i.e., if a **metal** alloy film is desired), the precursor composition can include more than one pyrazolyl complex. Alternatively, various percursor compositions can be. . .

DETD . . . gases that are generally unreactive with the pyrazolyl complexes described herein and do not interfere with the formation of a **metal**-containing film. Examples include nitrogen, helium, argon, and mixtures thereof. The reaction gas can be selected from a wide variety of. . .

DETD The designation "pyrazolyl complex" refers to a **metal** complex containing one or more anionic pyrazolyl ligands. Any of a variety of pyrazolyl ligands can be present in the. . . long as the complex can be used to form a film using chemical vaporization techniques. The pyrazolyl ligand stabilizes the **metal** complex and can be tailored to yield desired solubility and viscosity characteristics. Preferably, the anionic pyrazolyl ligand has the following. . . (R.sup.1, R.sup.2, and R.sup.3) are each individually H, an organic group, or a halide. Such ligands can bond to a **metal** through one, two, or all three pyrazole groups.

DETD . . . aryloxy groups, and oxo groups. Preferably, the pyrazolyl complex includes one or more ligands of Formula I attached to a **metal** selected from the group of the Group IIA metals (i.e., Group 2 or alkaline earth metals), the Group IVB metals. . . y is 2 to 5 (preferably, 3 or 4). These complexes are monomers (i.e., mononuclear) in that they contain one **metal** per molecule.

DETD . . . In the context of the present invention, the organic groups are those that do not interfere with the formation of **metal** -containing film. Preferably, they are of a type and size that do not interfere with the formation of a **metal**-containing film using chemical vapor deposition techniques. The term "aliphatic group" means a saturated or unsaturated linear or branched hydrocarbon group.. . .

DETD . . . t-butyl, and the like, but also alkyl substituents bearing further substituents known in the art, such as hydroxy, alkoxy, alkylsulfonyl, **halogen** atoms, cyano, nitro, amino, carboxyl, etc. Thus, "alkyl group" includes ether groups, haloalkyls, nitroalkyls, carboxyalkyls, hydroxyalkyls, sulfoalkyls, etc. On the. . .

DETD In the pyrazolyl complexes of Formulas II-V, M refers to a **metal** of Groups IIA (alkaline earth metals), IVB (the titanium group), VA (Bi), and VB (the vanadium group). Preferred metals M. . .

DETD . . . Formulas II-IV of the present invention can be prepared by reaction of the above lithium pyrazolyl methanate with the appropriate **metal** halide (e.g., BaI.sub.2, SrI.sub.2, Ti(OR).sub.2 Cl.sub.2).

DETD . . . Formulas II-V. Such preferred precursor compositions can also include complexes of Groups IIA, IVB, VA, and VB metals or other **metal** or metalloid complexes that do not include the ligand of Formula I, as long as there is at least one. . .

DETD Methods of the present invention can be used to deposit a **metal** -containing film, preferably an oxide film, on a variety of substrates, such as a semiconductor wafer (e.g., silicon wafer, gallium arsenide.

. . that is not detrimental to the substrate, other layers thereon, etc. Preferably, however, solvents are not used; rather, the transition **metal** complexes are liquid and used neat. Methods of the present invention preferably utilize vapor deposition techniques, such as flash vaporization,. . .

DETD In this process, the precursor composition 40, which contains one or more pyrazolyl complexes (and/or other **metal** or metalloid complexes), is stored in liquid form (a neat liquid at room temperature or at an elevated temperature if. . .

DETD In this process, one or more solutions 60 of one or more pyrazolyl precursor complexes (and/or other **metal** or metalloid complexes), are stored in vessels 62. The solutions are transferred to a mixing manifold 64 using pumps 66.. . .

DETD . . . 2 and 4 are prepared by dissolving the solid compounds in THF to make 0.1 M solutions in the respective **metal**. The solutions are separately delivered to a vaporizer (COVA Technologies, Inc., Colorado Springs, Colo.) using syringe pumps. From here, the. . .

DETD . . . 2-4 are prepared by dissolving the solid compounds in THF to make 0.05M, 0.05M, and 0.1M solutions in the respective **metal**. The solutions are separately delivered to a vaporizer (COVA Technologies, Inc., Colorado Springs, Colo.) using syringe pumps. From here, the. . .

CLM What is claimed is:

. . . manufacturing a semiconductor structure comprising: providing a semiconductor substrate or substrate assembly; providing a precursor composition comprising one or more **metal** complexes comprising a Group IIA, IVB, VA, or VB **metal** and one or more anionic tris(pyrazolyl)methanate ligands of the formula: ##STR3## wherein each R.sup.1, R.sup.2, and R.sup.3 group is independently. . . composition and directing it toward the semiconductor substrate or substrate assembly using a chemical vapor deposition technique to form a **metal**-containing film on a surface of the semiconductor substrate or substrate assembly.

7. The method of claim 1 wherein the precursor composition comprises a solid **metal** complex dissolved in an organic solvent.

9. The method of claim 1 wherein the **metal** is selected from the group of Ba, Sr, Ti, and mixtures thereof.

. . . M(OR.sup.4).sub.x L.sub.4-x, and M(OR.sup.4).sub.y L.sub.5-y, wherein L is the anionic tri(pyrazolyl)methanate ligand, M is a Group IIA, IVB,

or VB **metal**, R.sup.4 is an organic group, x=2 to 4, and y=2 to 5.

11. The method of claim 1 wherein the precursor composition further comprises one or more **metal** complexes that do not contain the anionic tris(pyraxolyl)methanate ligand.

. . . . manufacturing a semiconductor structure comprising: providing a semiconductor substrate or substrate assembly; providing a precursor composition comprising one or more **metal** complexes selected from the group of ML.sub.2, M(O)L.sub.2, M(OR.sup.4).sub.x L.sub.4-x, and M(OR.sup.4).sub.y L.sub.5-y ; wherein: M is a Group IIA, IVB, VA, or VB **metal**; each R.sup.4 group is independently an organic group; x=2 to 4; y=2 to 5; L is an anionic ligand of. . . composition and directing it toward the semiconductor substrate or substrate assembly using a chemical vapor deposition technique to form a **metal**-containing film on a surface of the semiconductor substrate or substrate assembly.

. . . . memory device structure comprising: providing a substrate having a first electrode thereon; providing a precursor composition comprising one or more **metal** complexes comprising a Group IIA, IVB, VA, or VB **metal** and one or more anionic tris(pyrazolyl)methanate ligands of the formula: ##STR5## wherein each R.sup.1, R.sup.2, and R.sup.3 group is independently. . .

. . . . memory device structure comprising: providing a substrate having a first electrode thereon; providing a precursor composition comprising one or more **metal** complexes selected from the group of ML.sub.2, M(O)L.sub.2, M(OR.sup.4).sub.x L.sub.4-x, and M(OR.sup.4).sub.y L.sub.5-y ; wherein: M is a Group IIA, IVB, VA, or VB **metal**; each R.sup.4 group is independently an organic group; x=2 to 4; y=2 to 5; L is an anionic ligand of. . .

. . . . method of forming a film on a substrate comprising: providing a substrate; providing a precursor composition comprising one or more **metal** complexes comprising a Group IIA, IVB, VA, or VB **metal** and one or more anionic tris(pyrazolyl)methanate ligands of the formula: ##STR7## wherein each R.sup.1, R.sup.2, and R.sup.3 group is independently. . . and vaporizing the precursor composition and directing it toward the substrate using a chemical vapor deposition technique to form a **metal**-containing film on the substrate.

. . . . method of forming a film on a substrate comprising: providing a substrate; providing a precursor composition comprising one or more **metal** complexes selected from the group of ML.sub.2, M(O)L.sub.2, M(OR.sup.4).sub.x L.sub.4-x, and M(OR.sup.4).sub.y L.sub.5-y ; wherein: M is a Group IIA, IVB, VA, or VB **metal**; each R.sup.4 group is independently an organic group; x=2 to 4; y=2 to 5; L is an anionic ligand of. . . and vaporizing the precursor composition and directing it toward the substrate using a chemical vapor deposition technique to form a **metal**-containing film on the substrate.

. . . . of forming a film on a substrate comprising: providing a substrate; providing a liquid precursor composition comprising one or more **metal** complexes comprising a Group IIA, IVB, VA, or VB **metal** and one or more anionic tris(pyrazolyl)methanate ligands of the formula: ##STR9## wherein each R group is independently H, an

organic. . .
. . . . of forming a film on a substrate comprising: providing a substrate; providing a liquid precursor composition comprising one or more **metal** complexes selected from the group of ML.sub.2, M(O)L.sub.2, M(OR.sup.4).sub.x L.sub.4-x, and M(OR.sup.4).sub.y L.sub.5-y ; wherein: M is a Group IIA, IVB, VA, or VB **metal**; each R.sup.4 group is independently an organic group; x=2 to 4; y=2 to 5; L is an anionic ligand of. . .

IT 20717-86-6, Titanium chlorotris(isopropoxide) **28791-97-1** **28791-97-1D**, metal complexes
(prepn. and reactions of lithium tris(dimethylpyrazolyl)methanate in prepn. of ligands for OMCVD)

L14 ANSWER 9 OF 16 USPATFULL

ACCESSION NUMBER: 2000:131664 USPATFULL
TITLE: Complexes having tris (pyrazolyl) borate ligands for forming films
INVENTOR(S): Uhlenbrock, Stefan, Boise, ID, United States
Vaartstra, Brian A., Nampa, ID, United States
PATENT ASSIGNEE(S): Micron Technology, Inc., Boise, ID, United States (U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 6127192		20001003	
APPLICATION INFO.:	US 1998-141432		19980827	(9)

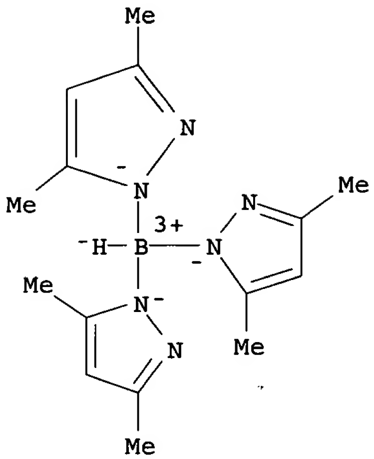
DOCUMENT TYPE: Utility
FILE SEGMENT: Granted
PRIMARY EXAMINER: Nelms, David
ASSISTANT EXAMINER: Nhu, David
LEGAL REPRESENTATIVE: Mueting, Raasch & Gebhardt, P.A.
NUMBER OF CLAIMS: 32
EXEMPLARY CLAIM: 1
NUMBER OF DRAWINGS: 3 Drawing Figure(s); 3 Drawing Page(s)
LINE COUNT: 785
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Methods of forming a film on a substrate using chemical vapor deposition techniques and pyrazolyl complexes. The complexes and methods are particularly suitable for the preparation of semiconductor structures.

IT **155476-96-3 157044-88-7**
(complexes having tris(pyrazolyl) borate ligands for forming films by OMCVD in semiconductor device fabrication)

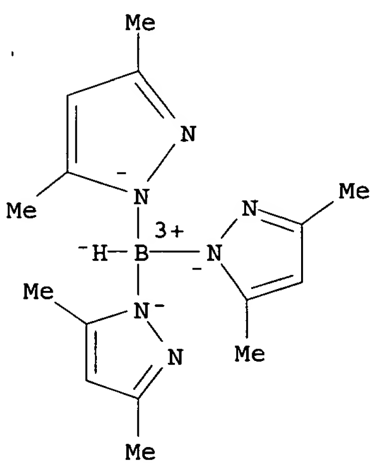
RN 155476-96-3 USPATFULL

CN Borate(1-), tris(3,5-dimethyl-1H-pyrazolato-.kappa.N1)hydro-, barium (2:1), (T-4)- (9CI) (CA INDEX NAME)



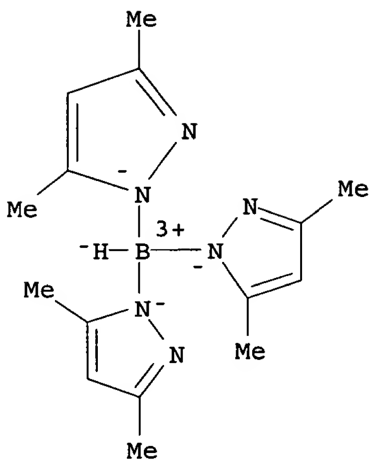
●1/2 Ba^{2+}

RN 157044-88-7 USPATFULL
CN Borate(1-), tris(3,5-dimethyl-1H-pyrazolato-.kappa.N1)hydro-, strontium (2:1), (T-4)- (9CI) (CA INDEX NAME)



●1/2 Sr^{2+}

IT **17567-17-8**
(in prepn. of tris(pyrazolyl) borate complex)
RN 17567-17-8 USPATFULL
CN Borate(1-), tris(3,5-dimethyl-1H-pyrazolato-.kappa.N1)hydro-, potassium, (T-4)- (9CI) (CA INDEX NAME)



$\bullet$ K^+

SUMM This invention relates to methods of depositing films, such as **metal** oxide films, especially barium-strontium-titanate (BST) films on substrates, particularly semiconductor device structures.

SUMM . . . random access memory (SRAM) devices, and now ferroelectric memory (FE RAM) devices. They consist of two conductors, such as parallel **metal** or polysilicon plates, which act as the electrodes (i.e., the storage node electrode and the cell plate capacitor electrode), insulated. . .

SUMM Suitable **metal** oxides are typically delivered to a substrate in the vapor phase; however, many oxides are difficult to deliver using vapor. . .

SUMM The present invention is directed to complexes and methods for forming **metal**-containing films on substrates, such as semiconductor substrates or substrate assemblies during the manufacture of semiconductor structures, particularly memory devices. The. . . having one or more tris(pyrazolyl)borate ligands (referred to herein as pyrazolyl complexes). Typically and preferably, the film is a dielectric **metal**-containing material. The **metal**-containing film can be an oxide, sulfide, selenide, telluride, nitride, or combination thereof, for example. Preferably, the film is a **metal** -containing oxide film. The film can be used as a dielectric layer in an integrated circuit structure, particularly in a memory. . .

SUMM . . . toward a substrate, such as a semiconductor substrate or substrate assembly, using a chemical vapor deposition technique to form a **metal**-containing film on a surface of the substrate, wherein the pyrazolyl complex includes one or more anionic tris(pyrazolyl)borate ligands of the. . . H or an organic group). Preferably, the pyrazolyl complex includes one or more ligands of Formula I attached to a **metal** selected from the group of the Group IIA (i.e., Group 2) metals, the Group IVB (i.e., Group 4) metals, the. . . or 4). For certain of the preferred embodiments, the precursor composition includes at least one pyrazolyl complex that includes a **metal** selected

from the group of Zr, Hf, V, Nb, and Ta.

DETD . . . present invention provides a method of forming a film (preferably, an oxide film) using one or more pyrazolyl complexes (i.e., **metal** complexes containing one or more tris(pyrazolyl)borate ligands). Preferably, the pyrazolyl complexes are mononuclear (i.e., monomers) and display few intermolecular forces. . .

DETD . . . vaporizing a precursor composition, preferably a liquid precursor composition, that includes one or more pyrazolyl complexes. If more than one **metal** is desired in the resulting **metal** -containing film (i.e., if a **metal** alloy film is desired), the precursor composition can include more than one pyrazolyl complex. Alternatively, various percursor compositions can be. . .

DETD . . . gases that are generally unreactive with the pyrazolyl complexes described herein and do not interfere with the formation of a **metal**-containing film. Examples include nitrogen, helium, argon, and mixtures thereof. The reaction gas can be selected from a wide variety of. . .

DETD The designation "pyrazolyl complex" refers to a **metal** complex containing one or more anionic pyrazolyl ligands. Any of a variety of pyrazolyl ligands can be present in the. . . long as the complex can be used to form a film using chemical vaporization techniques. The pyrazolyl ligand stabilizes the **metal** complex and can be tailored to yield desired solubility and viscosity characteristics. Preferably, the anionic pyrazolyl ligand has the following. . . or a halide, and preferably, the R.sup.4 group is H or an organic group. Such ligands can bond to a **metal** through one, two, or all three pyrazole groups.

DETD . . . aryloxy groups, and oxo groups. Preferably, the pyrazolyl complex includes one or more ligands of Formula I attached to a **metal** selected from the group of the Group IIA metals (i.e., Group 2 or alkaline earth metals), the Group IVB metals. . . y is 2 to 5 (preferably, 3 or 4). These complexes are monomers (i.e., mononuclear) in that they contain one **metal** per molecule.

DETD . . . the context of the present invention, the organic groups are those that do not interfere with the formation of a **metal** -containing film. Preferably, they are of a type and size that do not interfere with the formation of a **metal**-containing film using chemical vapor deposition techniques. The term "aliphatic group" means a saturated or unsaturated linear or branched hydrocarbon group.. . .

DETD . . . t-butyl, and the like, but also alkyl substituents bearing further substituents known in the art, such as hydroxy, alkoxy, alkylsulfonyl, **halogen** atoms, cyano, nitro, amino, carboxyl, etc. Thus, "alkyl group" includes ether groups, haloalkyls, nitroalkyls, carboxyalkyls, hydroxyalkyls, sulfoalkyls, etc. On the. . .

DETD In the pyrazolyl complexes of Formulas II-V, M refers to a **metal** of Groups IIA (alkaline earth metals), IVB (the titanium group), VA (Bi), and VB (the vanadium group). Preferred metals M. . .

DETD . . . pyrazolyl complexes of Formulas II-V of the present invention can be prepared by the above potassium pyrazolate with the appropriate **metal** halide (e.g., BaI.sub.2, SrI.sub.2, or Ti(OR).sub.2 Cl.sub.2).

DETD . . . Formulas II-V. Such preferred precursor compositions can also include complexes of Groups IIA, IVB, VA, and VB metals or other **metal** or metalloid complexes that do not include the ligand of Formula I, as long as there is at least one. . .

DETD Methods of the present invention can be used to deposit a **metal** -containing film, preferably an oxide film, on a variety of substrates, such as a semiconductor wafer (e.g., silicon wafer, gallium arsenide.

.

. that is not detrimental to the substrate, other layers thereon, etc. Preferably, however, solvents are not used; rather, the transition **metal** complexes are liquid and used neat. Methods of the present invention preferably utilize vapor deposition techniques, such as flash vaporization,. . .

DETD In this process, the precursor composition 40, which contains one or more pyrazolyl complexes (and/or other **metal** or metalloid complexes), is stored in liquid form (a neat liquid at room temperature or at an elevated temperature if. . .

DETD In this process, one or more solutions 60 of one or more pyrazolyl precursor complexes (and/or other **metal** or metalloid complexes), are stored in vessels 62. The solutions are transferred to a mixing manifold 64 using pumps 66.. . .

DETD . . . 1-3 are prepared by dissolving the solid compounds in THF to make 0.05M, 0.05M, and 0.1M solutions in the respective **metal**. The solutions are separately delivered to a vaporizer (COVA Technologies, Inc., Colorado Springs, Colo.) using syringe pumps. From here, the. . .

CLM What is claimed is:

. . . . or substrate assembly; providing a precursor composition comprising two or more complexes comprising a Group IIA, IVB, VA, or VB **metal** and one or more anionic tris(pyrazolyl)borate ligands of the formula: ##STR3## wherein each R.sup.1, R.sup.2, R.sup.3, and R.sup.4 group is. . . composition and directing it toward the semiconductor substrate or substrate assembly using a chemical vapor deposition technique to form a **metal**-containing film on a surface of the semiconductor substrate or substrate assembly.

7. The method of claim 1 wherein the precursor composition comprises a solid **metal** complex dissolved in an organic solvent.

9. The method of claim 1 wherein the **metal** is selected from the group of Ba, Sr, Ti, and mixtures thereof.

. . . . and M(OR.sup.5).sub.y L.sub.5-y ; wherein L is the anionic tris(pyrazolyl)borate ligand, M is a Group IIA, IVB, VA, or VB **metal**, R.sup.5 is an organic group, x=2 to 4, and y=2 to 5.

11. The method of claim 1 wherein the precursor composition further comprises one or more **metal** complexes that do not contain the anionic tris(pyrazolyl)borate ligand.

. . . . group of ML.sub.2, M(O)L.sub.2, M(OR.sup.5).sub.x L.sub.4-x, and M(OR.sup.5).sub.y L.sub.5-y ; wherein: M is a Group IIA, IVB, VA, or VB **metal**; each R.sup.5 group is independently an organic group; x=2 to 4; y=2 to 5; L is an anionic ligand of. . . composition and directing it toward the semiconductor substrate or substrate assembly using a chemical vapor deposition technique to form a **metal** -containing film on a surface of the semiconductor substrate or substrate assembly.

. . . . or substrate assembly; providing a precursor composition comprising one or more complexes comprising a Group IIA, IVB, VA, or VB **metal**, with the proviso that at least one of the complexes includes a **metal** selected from the group of Zr, Hf, V, Nb, and

Ta, and one or more anionic tris(pyrazolyl)borate ligands of the. . . composition and directing it toward the semiconductor substrate or substrate assembly using a chemical vapor deposition technique to form a **metal**-containing film on a surface of the semiconductor substrate or substrate assembly.

. . . first electrode thereon; providing a precursor composition comprising two or more complexes comprising a Group IIA, IVB, VA, or VB **metal** and one or more anionic tris(pyrazolyl)borate ligands of the formula: ##STR6## wherein each R.sup.1, R.sup.2, R.sup.3, and R.sup.4 group is. . .
. . . group of ML.sub.2, M(O)L.sub.2, M(OR.sup.5).sub.x L.sub.4-x, and M(OR.sup.5).sub.y L.sub.5-y ; wherein: M is a Group IIA, IVB, VA, or VB **metal**; each R.sup.5 group is independently an organic group; x=2 to 4; y=2to5; L is an anionic ligand of the following. . .
. . . first electrode thereon; providing a precursor composition comprising one or more complexes comprising a Group IIA, IVB, VA, or VB **metal**, with the proviso that at least one of the complexes includes a **metal** selected from the group of Zr, Hf, V, Nb, and Ta, and one or more anionic tris(pyrazolyl)borate ligands of the. . .
. . . providing a substrate; providing a precursor composition comprising two or more complexes comprising a Group IIA, IVB, VA, or VB **metal** and one or more anionic tris(pyrazolyl)borate ligands of the formula: ##STR9## wherein each R.sup.1, R.sup.2, R.sup.3, and R.sup.4 group is. . . and vaporizing the precursor composition and directing it toward the substrate using a chemical vapor deposition technique to form a **metal**-containing film on the substrate.

. . . group of ML.sub.2, M(O)L.sub.2, M(OR.sup.5).sub.x L.sub.4-x, and M(OR.sup.5).sub.y L.sub.5-y ; wherein: M is a Group IIA, IVB, VA, or VB **metal**; each R.sup.5 group is independently an organic group; x=2 to 4; y=2 to 5; L is an anionic ligand of. . . and vaporizing the precursor composition and directing it toward the substrate using a chemical vapor deposition technique to form a **metal**-containing film on the substrate.

. . . providing a substrate; providing a precursor composition comprising one or more complexes comprising a Group IIA, IVB, VA, or VB **metal**, with the proviso that at least one complex includes a **metal** selected from the group of Zr, Hf, V, Nb, and Ta, and one or more anionic tris(pyrazolyl)borate ligands of the. . . and vaporizing the precursor composition and directing it toward the substrate using a chemical vapor deposition technique to form a **metal**-containing film on the substrate.

. . . a substrate; providing a liquid precursor composition comprising two or more complexes comprising a Group IIA, IVB, VA, or VB **metal** and two or more anionic tris(pyrazolyl)borate ligands of the formula: ##STR12## wherein each R.sup.1, R.sup.2, R.sup.3, and R.sup.4 group is. . . liquid precursor composition to form vaporized precursor composition; and directing the vaporized precursor composition toward the substrate to form a **metal**-containing film on the substrate.

. . . group of ML.sub.2, M(O)L.sub.2, M(OR.sup.5).sub.x L.sub.4-x, and M(OR.sup.5).sub.y L.sub.5-y ; wherein: M is a Group IIA, IVB, VA, or VB **metal**; each R.sup.5 group is independently an organic group; x=2

to 4; y=2 to 5; L is an anionic ligand of. . . liquid precursor composition to form vaporized precursor composition; and directing the vaporized precursor composition toward the substrate to form a **metal**-containing film on the substrate.

. . . . a substrate; providing a liquid precursor composition comprising one or more complexes comprising a Group IIA, IVB, VA, or VB **metal** , with the proviso that at least one of the complexes includes a **metal** selected from the group of Zr, Hf, V, Nb, and Ta, and two or more anionic tris(pyrazolyl)borate ligands of the. . . liquid precursor composition to form vaporized precursor composition; and directing the vaporized precursor composition toward the substrate to form a **metal**-containing film on the substrate.

IT **155476-96-3 157044-88-7** 157072-65-6 158444-73-6
(complexes having tris(pyrazolyl) borate ligands for forming films by OMCVD in semiconductor device fabrication)
IT **17567-17-8**
(in prepn. of tris(pyrazolyl) borate complex)

L14 ANSWER 10 OF 16 USPATFULL
ACCESSION NUMBER: 2000:67699 USPATFULL
TITLE: Bis- and tris(pyrazolyl)borate **metal** complex catalysts
INVENTOR(S): Klaui, Wolfgang, Bloemendalstraat, Switzerland
Domhover, Bernd, Gelsenkirchen, Germany, Federal Republic of
PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Ludwigshafen, Germany, Federal Republic of (non-U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 6069110		20000530	
	WO 9723492		19970703	
APPLICATION INFO.:	US 1998-91285		19980616	(9)
	WO 1996-EP5715		19961219	
			19980616	PCT 371 date
			19980616	PCT 102(e) date

	NUMBER	DATE
PRIORITY INFORMATION:	DE 1995-19548146	19951221

DOCUMENT TYPE: Utility
FILE SEGMENT: Granted
PRIMARY EXAMINER: Gupta, Yogendra
ASSISTANT EXAMINER: Webb, Gregory E.
LEGAL REPRESENTATIVE: Keil & Weinkauf
NUMBER OF CLAIMS: 9
EXEMPLARY CLAIM: 1
LINE COUNT: 558
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB **Metal** complexes of the formula (I) or (I') are suitable for the oligomerization and polymerization of olefinically unsaturated compounds and for the copolymerization thereof with carbon monoxide ##STR1## M is a **metal** from sub-group eight of the Periodic Table of the Elements, E is an element from main group five of the Periodic Table of the Elements,

R.sup.1 to R.sup.11, R.sup.15 are substituents selected from the group

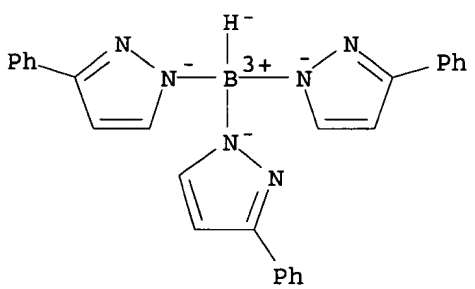
consisting of hydrogen, C.sub.1 - to C.sub.30 -organocarbon radicals and
C.sub.3 - to C.sub.30 -organosilicon radicals, and

R.sup.12 to R.sup.14 are substituents selected from the group consisting
of C.sub.1 - to C.sub.30 -organocarbon radicals and C.sub.3 - to
C.sub.30 -organosilicon radicals.

IT **106210-02-0**
(complex precursor; bis- and tris(pyrazolyl)borate metal complex catalysts and their manuf. for oligomerization and polymn. of olefins)

RN 106210-02-0 USPATFULL

CN Borate(1-), hydrotris(3-phenyl-1H-pyrazolato-.kappa.N1)-, thallium(1+), (T-4)- (9CI) (CA INDEX NAME)



● Tl(I) +

TI Bis- and tris(pyrazolyl)borate **metal** complex catalysts

AB **Metal** complexes of the formula (I) or (I') are suitable for the oligomerization and polymerization of olefinically unsaturated compounds and for the copolymerization thereof with carbon monoxide ##STR1## M is a **metal** from sub-group eight of the Periodic Table of the Elements, E is an element from main group five of the. . .

SUMM The present invention relates to **metal** complexes of the formulae (I) and (I') which are suitable for the oligomerization and polymerization of olefinically unsaturated compounds and for the copolymerization thereof with carbon monoxide ##STR2## where M is a **metal** from sub-group eight of the Periodic Table of the Elements,

SUMM A) a **metal** complex of the formula (I) ##STR3## or a **metal** complex of the formula (I') ##STR4## where M is a **metal** from sub-group eight of the Periodic Table of the Elements,

SUMM The present invention furthermore relates to a process for the preparation of **metal** complexes of the formula (I) ##STR5## by reacting a halometal complex of the **metal** with a tris(pyrazolyl)borate anion of the formula (II) ##STR6## or with a bis(pyrazolyl)borate anion of the formula (II') ##STR7## where, in (I), (I'), (II) or (II'), M is a **metal** from sub-group eight of the Periodic Table of the Elements,

SUMM . . . polymerizing the monomers at from 0 to 300.degree. C. and from 1 to 500,000 kPa in the presence of a **metal** complex of the formula (I) ##STR8## where M is a **metal** from sub-group eight

of the Periodic Table of the Elements,

SUMM A) a **metal** complex of the formula (I) ##STR9## where M is a **metal** from sub-group eight of the Periodic Table of the elements,

SUMM The present invention furthermore relates to the use of a **metal** complex of the formulae (I) and (I') as claimed in claim 1 as catalyst for the preparation of oligomers and. . .

SUMM **Metal** complexes of metals from sub-group eight of the Periodic Table of the Elements have hitherto, such as nickel, been used. . .

SUMM However, none of the **metal** complexes or catalysts employed was free from disadvantages; either they were complicated to prepare, expensive, had unsatisfactory activity or required. . .

SUMM It is an object of the present invention to provide **metal** complexes of the formulae (I) and (I') and catalyst systems containing (I) or (I') which do not have the abovementioned. . . are easily accessible. A further object of the present invention was to provide a process for the preparation of the **metal** complexes of the formulae (I) and (I') and a process for the preparation of oligomers and polymers of olefinically unsaturated. . . and a process for the preparation of copolymers of olefinically unsaturated compounds and carbon monoxide in the presence of the **metal** complexes of the formulae (I) and (I') or in the presence of the catalyst systems, and the use of the **metal** complexes of the formula (I) or (I') or of the catalyst systems for the preparation of oligomers and polymers of. . .

SUMM We have found that this object is achieved by the **metal** complexes of the formulae (I) and (I') defined at the outset and by the catalyst systems defined at the outset, by a process for the preparation of the **metal** complexes of the formulae (I) and (I'), by a process for the preparation of oligomers and polymers of olefinically unsaturated compounds and of copolymers of olefinically unsaturated compounds and carbon monoxide in the presence of the **metal** complexes of the formulae (I) or (I') or in the presence of the catalyst systems defined at the outset, and by the use of the **metal** complexes of the formulae (I) and (I') and by the use of the catalyst systems defined at the outset for. . .

SUMM Suitable metals M in the **metal** complexes of the formulae (I) and (I') are those from sub-group eight (VIIIB) of the Periodic Table of the Elements,. . .

SUMM **Metal** complexes of the formulae (I) and (I') which have proven very highly suitable are those in which R.sup.11, R.sup.12, R.sup.13,. . .

SUMM Examples of very particularly preferred **metal** complexes of the formulae (I) and (I') are

SUMM A particularly preferred **metal** complex of the formula (I') is [{dihydrobis(3-phenylpyrazolyl)borato}(ortho-tolyl)(triphenylphosphine)]nickel(II).

SUMM It has proven advantageous to react the novel **metal** complexes of the formulae (I) and (I') with a compound B) which is capable of binding the ligand ER.sup.12 R.sup.13 R.sup.14 more strongly than can the **metal** M.

SUMM As component A), the catalyst systems can of course also contain mixtures of different **metal** complexes of the formula (I) or (I').

SUMM The novel **metal** complexes of the formulae (I) and (I') are advantageously prepared by substitution of a **halogen** atom,

i.e. fluorine, chlorine, bromine or iodine, in a **halogen-metal** complex of the metals M by a bis- or tris(pyrazolyl)borato ligand.

SUMM To this end, a main-group **metal** compound of the formula (II) ##STR10## where M' is lithium, sodium, potassium, rubidium, cesium, magnesium, calcium or preferably thallium, n,. . . 2, and R.sup.1 to R.sup.15 are as specified above under the formulae (I) or (I'), is usually reacted with a **halogen-metal** complex of the **metal** M, in particular of nickel or palladium, preferably in an organic solvent, such as dichloromethane, toluene, tetrahydrofuran or diethyl ether.

SUMM Mixtures of solvents, for example acetone/dichloromethane, are also preferably used for the preparation of the **metal** complexes of the formula (I').

SUMM The **halogen-metal** complex used is preferably one of the formula M(ER.sup.12 R.sup.13 R.sup.14).sub.2 (R.sup.11).times.(III), where M, E and R.sup.11 to R.sup.14 are. . .

SUMM The novel **metal** complexes of the formula (I) or (I') and the catalyst systems can be used for the preparation of oligomers and. . .

SUMM Polymerization reactions using the **metal** complexes of the formula (I) or (I') or catalyst systems defined at the outset can be carried out in the. . .

CLM What is claimed is:

1. A **metal** complex of the formula (I) or (I') which is suitable for the oligomerization and polymerization of olefinically unsaturated compounds and for the copolymerization thereof with carbon monoxide ##STR11## where M is a **metal** from sub-group eight of the Periodic Table of the Elements, E is an element from main group five of the. . .

. . . . oligomerization and polymerization of olefinically unsaturated compounds and the copolymerization thereof with carbon monoxide, comprising, as active constituents, A) a **metal** complex of the formula (I) ##STR12## or a **metal** complex of the formula (I') ##STR13## where M is a **metal** from sub-group eight of the Periodic Table of the Elements, E is an element from main group five of the. . .

3. A process for the preparation of a **metal** complex of the formula (I) ##STR14## by reacting a halometal complex of the **metal** with a tris-(pyrazolyl)borate anion of the formula (II) ##STR15## or with a bis(pyrazolyl)borate anion of the formula (II') ##STR16## where, in (I), (I'), (II) or (II'), M is a **metal** from sub-group eight of the Periodic Table of the Elements, M' is lithium, sodium, potassium, rubidium, cesium, magnesium, calcium or. . .

. . . . polymerizing the monomers at from 0 to 300.degree. C. and from 1 to 500,000 kPa in the presence of a **metal** complex of the formula (I) ##STR17## where M is a **metal** from sub-group eight of the Periodic Table of the Elements, E is an element from main group five of the. . .

. . . . C. and from 1 to 500,000 kPa in the presence of a catalyst system comprising, as active constituents, A) a **metal** complex of the formula (I) ##STR18## where M is a **metal** from sub-group eight of the Periodic Table of the Elements, E is an element from main group five of the. . .

6. A **metal** complex of the formula (I) or (I') which is suitable for the oligomerization and polymerization of olefinically unsaturated compounds and. . .

7. A **metal** complex as claimed in claim 6, where R.sup.3, R.sup.6, R.sup.9 and R.sup.11 to R.sup.14 are C.sub.6 - to C.sub.20 -aryl. . . .
8. A **metal** complex of the formula (I) or (I') which is suitable for the oligomerization and polymerization of olefinically unsaturated compounds and for the copolymerization thereof with carbon monoxide ##STR20## where M is a **metal** from sub-group eight of the Periodic Table of the Elements, E is an element from main group five of the. . . .
9. A **metal** complex as claimed in claim 8, where R.sup.3, R.sup.6, R.sup.9 and R.sup.12 to R.sup.14 are C.sub.6 - to C.sub.20 -aryl. . . .

IT 30112-17-5 **106210-02-0** 107599-10-0
(complex precursor; bis- and tris(pyrazolyl)borate metal complex catalysts and their manuf. for oligomerization and polymn. of olefins)

L14 ANSWER 11 OF 16 USPATFULL
ACCESSION NUMBER: 1999:78905 USPATFULL
TITLE: Method for producing dimerization product of acrylonitrile
INVENTOR(S): Suzuki, Yasuhiko, Yamaguchi, Japan
Kiso, Yoshihisa, Yamaguchi, Japan
PATENT ASSIGNEE(S): Mitsui Chemicals, Inc., Tokyo, Japan (non-U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 5922901		19990713	
	WO 9701531		19970116	
APPLICATION INFO.:	US 1997-793491		19970226	(8)
	WO 1996-JP1760		19960626	
			19970226	PCT 371 date
			19970226	PCT 102(e) date

	NUMBER	DATE
PRIORITY INFORMATION:	JP 1995-164339	19950629

DOCUMENT TYPE: Utility
FILE SEGMENT: Granted
PRIMARY EXAMINER: Shah, Mukund J.
ASSISTANT EXAMINER: Ngo, Tamthom T.
LEGAL REPRESENTATIVE: Birch, Stewart, Kolasch & Birch, LLP
NUMBER OF CLAIMS: 17
EXEMPLARY CLAIM: 1
LINE COUNT: 434
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

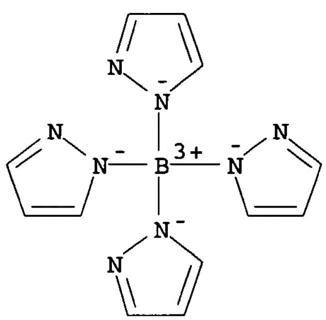
AB It is contemplated to provide an industrially adapted method for producing a dimerization product of acrylonitrile, which method is capable of producing a straight chain dimer of acrylonitrile efficiently at a high yield in a simple manner using a highly active catalyst exhibiting superior stability, without suffering from occurrence of difficulty removable by-products. In the method according to the present invention, acrylonitrile is subjected to dimerization in the presence of a ruthenium complex composed of a central atom of ruthenium and ligands including cyclopentadiene or its derivative coordinating thereto. The dimerization product, such as adiponitrile, 1,4-dicyanobutene or

1,4-dicyanobutadiene, is useful as an intermediate for producing hexamethylenediamine and adipic acid, both serving for the starting material of nylon 66, or as an intermediate for producing, for example, an antirusting agent and a vulcanization accelerator for rubbers.

IT **14695-83-1**
(prepn. of acrylonitrile dimers using ruthenium complex as dimerization catalyst)

RN 14695-83-1 USPATFULL

CN Borate(1-), tetrakis(1H-pyrazolato-.kappa.N2)-, sodium (9CI) (CA INDEX NAME)



● Na^+

SUMM . . . naphthyl, anthracenyl and biphenyl; alkoxyl groups having 1-6 carbon atoms, such as methoxy, ethoxy, propoxy, isopropoxy, butoxy and phenoxy; and **halogen** atoms, such as fluorine, chlorine, bromine and iodine.

SUMM . . . have further ligands including an olefin compound having 2-8 carbon atoms, such as ethylene, 2,5-norbonadiene, cyclooctadiene and acrylonitrile, and/or a **halogen** atom, such as fluorine, chlorine, bromine and iodine (in the following, a ruthenium complex having an olefin compound and a. . .

SUMM Beside the above-mentioned ligands of oxy-hydrocarbon group, olefin compound and **halogen** atom, other ligand(s) may be contained, including a phosphine compound, such as triphenylphosphine or diphenylphosphinoethane; a boron compound, such as. . .

SUMM In the case of using a type B ruthenium complex, a **metal** salt and/or a reducing agent may be used together with the ruthenium complex.
As the **metal** salt, there may be enumerated inorganic salts, such as potassium carbonate and sodium carbonate; organic salts, such as
sodium acetate; and boron salts, such as sodium tetraphenylborate, sodium tetra(perfluorophenyl)borate and sodium tetra(4-fluorophenyl)borate. These **metal** salts may be used either alone or in a mixture of two or more of them, wherein the amount thereof. . .

SUMM . . . tin compounds, organic germanium compounds, organic silicium compounds, organic boron compounds, organic aluminum compounds, hydrogenated boron compounds, hydrogenated aluminum compounds, **metal** hydrides and elementary metals. These reducing agents may be used either alone or in a mixture of two or more. . .

SUMM . . . solvent to be used in the dimerization, there may be enumerated aliphatic alcohols, such as methanol, ethanol, propanol and butanol; **halogen**-substituted aliphatic alcohols, such as CF.sub.3 CH.sub.2 OH and CCl.sub.3 CH.sub.2 OH; aromatic alcohols, such as phenol and cresol; organic acids,. . . .

CLM What is claimed is:

6. The method according to claim 1 or 2, wherein the ruthenium complex further comprises a **halogen** atom and/or an olefin compound coordinating to the central ruthenium atom.

7. The method according to claim 6, wherein the dimerization is carried out in the presence of a **metal** salt and/or a reducing agent.

. . . having 1-10 carbon atoms, an aryl group having 6-14 carbon atoms, an alkoxyl group having 1-6 carbon atoms, or a **halogen** atom.

. . . combine with each other to form a diene compound; and X is an olefin compound having 2-8 carbon atoms, a **halogen** atom, a phosphine compound, a boron compound, an alkyl group having 1-10 carbon atoms, or an aryl group having 6-14. . .

IT 143-66-8, Sodium tetraphenylborate 563-63-3, Silver acetate **14695-83-1** 25776-12-9, Sodium tetrakis(4-fluorophenyl)borate 68146-65-6, Sodium tetrakis(1-imidazolyl)borate 92361-49-4 96503-27-4 120883-04-7 120883-05-8 186841-44-1 186841-45-2 186841-46-3 186841-47-4 186841-48-5 186841-49-6 186841-50-9 186841-51-0
(prepn. of acrylonitrile dimers using ruthenium complex as dimerization catalyst)

L14 ANSWER 12 OF 16 USPATFULL

ACCESSION NUMBER: 1999:30830 USPATFULL

TITLE: **Metal** complexes as cysteine protease inhibitors

INVENTOR(S): Grinstaff, Mark W., Durham, NC, United States
Gray, Harry B., Pasadena, CA, United States
Meade, Thomas J., Altadena, CA, United States

PATENT ASSIGNEE(S): California Institute of Technology, Pasadena, CA, United States (U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 5880149		19990309	
APPLICATION INFO.:	US 1996-721872		19960927	(8)

	NUMBER	DATE
PRIORITY INFORMATION:	US 1995-4451P	19950928 (60)

DOCUMENT TYPE: Utility
FILE SEGMENT: Granted
PRIMARY EXAMINER: Nazario-Gonzalez, Porfirio
LEGAL REPRESENTATIVE: Flehr Hohbach Test Albritton & Herbert LLP, Trecartin, Richard F., Silva, Robin M.
NUMBER OF CLAIMS: 13
EXEMPLARY CLAIM: 1,9,10
LINE COUNT: 1396
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The invention relates to **metal** complexes used to bind proteins

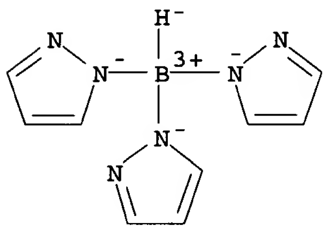
and enzymes.

IT **46755-84-4**

(for prepn. of Group 10 and 11 transition-metal Schiff-base complexes)

RN 46755-84-4 USPATFULL

CN Borate(1-), hydrotris(1H-pyrazolato-.kappa.N1)-, (T-4)- (9CI) (CA INDEX NAME)



TI **Metal** complexes as cysteine protease inhibitors

AB The invention relates to **metal** complexes used to bind proteins and enzymes.

SUMM The invention relates to **metal** complexes used to bind proteins and enzymes.

SUMM Three gold compounds have also been investigated and clinically used to treat arthritis (Dash **Metal** Ions Biol. Systm. 14:179 (1982); Elder et al., Chem. Rev. 87:1027 (1987)). These include Auranofin, a gold sodium thiomalate and. . .

SUMM The present invention provides **metal** complexes having the formula: ##STR2## wherein M is a transition **metal** ion selected from the group consisting of Cu, Ag, Au, Ni, Pd and Pt;

SUMM R.sub.1 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or may be absent when. . .

SUMM R.sub.2 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, carbonyl oxygen, phosphonyl oxygen, or. . .

SUMM R.sub.3 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, --OR.sub.5 when A is boron. . .

SUMM R.sub.4 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety;

SUMM R.sub.5 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety;

SUMM R.sub.6 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.7, may. . .

SUMM R.sub.7 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.6, may. . .

SUMM R.sub.8 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or may be absent when. . .

SUMM Further provided are **metal** complexes having the formula: ##STR3## wherein M is a transition **metal** ion selected from the group consisting of Cu, Ag, Au, Ni, Pd and Pt;

SUMM R.sub.9 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety;

SUMM R.sub.10 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety;

SUMM R.sub.11 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.12, may. . .

SUMM R.sub.12 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.11, may. . .

SUMM R.sub.13 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety;

SUMM R.sub.14 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety;

SUMM R.sub.15 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.16, may. . .

SUMM R.sub.16 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.15, may. . .

SUMM Also provided are **metal** complexes having the formula: ##STR4## wherein M is a transition **metal** ion selected from the group consisting of Cu, Ag, Au, Ni, Pd and Pt;

SUMM R.sub.17 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety;

SUMM R.sub.18 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety;

SUMM R.sub.19 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety;

SUMM R.sub.20 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.21, may. . .

SUMM R.sub.21 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.20, may. . .

SUMM R.sub.22 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.23, may. . .

SUMM R.sub.23 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.22, may. . .

SUMM R.sub.24 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety.

SUMM As is described below, the present invention is directed to **metal** compounds that can exchange or bind functional moieties such as cysteine on a protein's surface (e.g. in the active site. . . in the inactivation of a biological activity of the protein due to the complexing of the functional moiety to the **metal** compound.

SUMM Without being bound by theory, the **metal** complex compounds of the present invention derive their biological activity by the substitution or addition of ligands to the **metal** complexes. The biological activity of the complexes results from the binding of a new ligand, most preferably the sulfur atom of the side chain of cysteine. Presumably the amino acid serving as the new ligand of the **metal** complex is required by the target protein for its

biological activity. Thus, as is more fully described below, proteins such. . . cysteine proteases that utilize a cysteine in the active site, or proteins that use cysteines, for example, to bind essential **metal** ions, can be inactivated by the binding of the cysteine as a ligand of the **metal** complex, thus preventing the cysteine from participating in its normal biological function.

SUMM Accordingly, the addition of the **metal** complexes depicted herein are added to a protein or enzyme, for example, and one or more of the original ligands. . . ligands from the protein. This will occur either when the affinity of the protein axial ligand is higher for the **metal** complex as compared to the original ligand, or when the new axial ligand is present in elevated concentrations such that. . . protein. This latter possibility may be encouraged by the use of a targeting moiety, which increases the presence of the **metal** complex at the relevant site within the target protein or enzyme.

SUMM Alternative mechanisms of inhibition include the possibility that the **metal** complex oxidizes the free cysteines to form a disulfide bond in the active site. The enzyme remains inhibited until the disulfide bond is reduced, returning the activity. Thus, the possibility exists that the **metal** complexes depicted herein may be reversible inhibitors.

SUMM Alternatively, the **metal** complex may oxidize the free cysteine to cysteinic acid, or acts as a catalyst with oxygen present to produce reactive. . .

SUMM . . . acid" may serve as the new ligand. A "reactive amino acid" is one which is capable of binding to the **metal** compounds of the invention as a new ligand. Thus, while the sulfur atom of the side chain of cysteine is. . .

SUMM The present invention provides several classes of **metal** complexes which serve as cysteine protease inhibitors. Structure 1 generically depicts the first of such classes: ##STR6##

SUMM In this embodiment, M is a transition **metal** ion, A is either nitrogen or oxygen, E is oxygen, sulfur, nitrogen or selenium and D is carbon, boron (B) or phosphorus (P). X is either a counter-ion or a neutral coordinating ligand. R.sub.1 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or may be absent when A is oxygen, sulfur or selenium. R.sub.2 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, carbonyl oxygen, phosphonyl oxygen, or --OR.sub.5 when A is boron. R.sub.3 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, --OR.sub.5 when A is boron. . . or phosphorus, or is absent when R.sub.2 is carbonyl oxygen. R.sub.4, R.sub.5, R.sub.6, R.sub.7 and R.sub.8 are each independently hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety. In addition, R.sub.6 and. . .

SUMM Suitable transition **metal** ions prefer sulfur atoms as coordination atoms, and are selected from the group consisting of copper (including Cu+2 or Cu(II)),. . .

SUMM . . . choice of A, E, X and M will depend on a variety of factors. Since, in a preferred embodiment, the **metal** complexes of the invention are neutral, i.e. uncharged, the collective charge of the A, E, X and M moieties preferably. . .

SUMM . . . to, halogens; --OR; --SR; and --NHR, where R is a substituent

group as herein defined, preferably alkyl and aryl. By "**halogen**
" herein is meant F, Cl, Br, and I.
SUMM By "neutral coordinating ligand" herein is meant a neutral molecule capable of donating electrons to a **metal** to form a **metal**-ligand complex without a formal change in oxidation state. Suitable neutral coordinating ligands include, but are not limited to, water (H.sub.2. . .
SUMM . . . is meant a functional group that will specifically interact with the target protein, and thus is used to target the **metal** complex to a particular target protein. That is, the **metal** complex is covalently linked to a targeting moiety that will specifically bind or associate with a target protein. For example, the **metal** complexes of the invention may include a polypeptide inhibitor that is known to inhibit a protease, thus effectively increasing the local concentration of the **metal** complex at a functional site on the target protein. Suitable targeting moieties include, but are not limited to, polypeptides, nucleic. . .
SUMM In a preferred embodiment, the **metal** complex containing a targeting moiety as one of the R groups inhibits a protein, which may or
may not be. . . loss of enzymatic activity. For example, polypeptides
comprising protease substrates or inhibitors are used as an R group on the **metal** complexes, to form **metal** complexes that will selectively inhibit the protease. Similarly, a **metal** complex containing an R group comprising a nucleic acid that specifically binds to a particular nucleic acid binding protein such as a transcription factor is used to selectively inhibit the transcription factor. These targeted **metal** complexes preferentially bind to the target site on the protein, favoring that site over non-specific binding to other sites or. . .
SUMM In designing a **metal** complex for a particular protein, it is to be understood that the high affinity of the **metal** complex for a sulfur atom of cysteine or the other possible reactive moieties, is such that the **metal** complex need not be a perfect fit in the active site. Rather, what is important is that the **metal** complex be able to approach the target axial ligand moiety. For targeting active site residues of enzymes, for example, the **metal** complexes should generally not be larger than typical enzyme substrates or inhibitors. The gross structure and surface properties of the **metal** complex will determine its outer sphere interaction with the desired biological active site. Specificity in outer sphere interactions is optimized. . .
SUMM . . . (1992); Nielsen, Nature, 365:566 (1993)). These modifications of the ribose phosphate backbone may be done to facilitate the addition of **metal** complexes or to increase the stability and half-life of such molecules in physiological environments.
SUMM The polypeptide and the site of attachment of the polypeptide to the **metal** complex, will be chosen to maximize the interaction of the **metal** with the active site cysteine. That is, as is explained below, the polypeptide may be attached to the **metal** complex at the N-terminal or C-terminal end.
SUMM . . . substrate (or inhibitor) binding site. Thus, in a preferred embodiment, the polypeptide is chosen to allow optimum interaction of the **metal** complex with the active site cysteine. For example, the polypeptide may comprise roughly the P4 through P1 residues of a.
.
. the S4 to S1 positions of the enzyme's binding site), and be attached
at the C-terminal end (P1) to the **metal** complex, to maximize

the steric interaction of the **metal** complex with the active site of the enzyme, and particularly the active site cysteine. Alternatively, the polypeptide may comprise the. . . above, the interaction need not be perfect to allow inhibition, since it appears that increasing the local concentration of the **metal** complex near the active site is sufficient.

SUMM . . . variety of enzyme substrates and inhibitors for a variety of proteases containing either an active site cysteine or an essential **metal** ion coordinated by a cysteine are known in the art. In addition, the morphological properties of enzymes for which the crystal structures are known are used to design appropriate **metal** complexes. Alternative embodiments utilize known characteristics about surface charge and hydrophobicity, and substrate and inhibitor specificity.

SUMM In a preferred embodiment, the K.sub.1 of the polypeptide inhibitor is decreased as a result of attachment to the **metal** complex. That is, the inhibitor becomes a better inhibitor as a result of the attachment of the **metal** complex. Thus, the **metal** complex is effective at lower concentrations since fewer molecules are wasted at other sites.

SUMM In a preferred embodiment, at least one of the R groups is a nucleic acid used to target the **metal** complex to a particular protein or enzyme. For example, the target protein can be a nucleic acid binding protein that. . .

SUMM As with the polypeptides, the **metal** complex can be attached to the nucleic acid in a variety of ways in a variety of positions; the actual. . . attachment site is chosen to maximize the interaction of a reactive amino acid such as cysteine that is essential for **metal** ion binding (or an active site cysteine) with the **metal** complex. In a preferred embodiment, the backbone of the nucleic acid is modified to contain a functional group that can be used for attachment to the **metal** complex. This functional group may be added to either the 5' or 3' end of the nucleic acid for example.. . . to the ribophosphate backbone at the 2' or 3' position, thus allowing the attachment of the nucleic acid to the **metal** complex at either the 5' or 3' end. These amine groups are then used to couple the nucleic acid to the **metal** complex. Alternatively, nucleotide dimers, containing phosphoramide, phosphorothioate, phosphorodithioate, or O-methylphosphoroamidite linkages may be made, and added to the nucleic acid. . .

SUMM In a preferred embodiment, the **metal** complexes of the invention have the formula depicted below in Structure 7: ##STR12##

SUMM In Structure 7, M is a transition **metal** ion selected from the group consisting of Cu, Ag, Au, Ni, Pd and Pt, and E is oxygen, sulfur, or selenium, with oxygen being preferred. R.sub.9, R.sub.10, R.sub.13, and R.sub.14 are independently hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety. R.sub.11 and R.sub.12 are independently hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together may form a cycloalkyl or aryl group. Similarly, R.sub.15 and R.sub.16 are independently hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together may form a. . .

SUMM In a preferred embodiment, the **metal** complexes of the invention have the formula depicted below in Structure 8: ##STR13##

SUMM In Structure 8, M is a transition **metal** ion selected from the

group consisting of Cu, Ag, Au, Ni, Pd and Pt, with Cu+2 and Ni+2 being preferred. E is oxygen, sulfur, or selenium, with oxygen being preferred. R.sub.17, R.sub.18, R.sub.19, and R.sub.24 independently hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety. It should also be. . . R.sub.17 and R.sub.17 ' and R.sub.18 and R.sub.18 '; preferably these are all hydrogen. R.sub.20 and R.sub.21 are independently hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or together may form a cycloalkyl or aryl group. R.sub.22 and R.sub.23 are independently hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or together may form a. . .

SUMM In a preferred embodiment, the **metal** complexes of the invention have the formula depicted below in Structure 9: ##STR14##

SUMM In Structure 9, M is a transition **metal** ion with an oxidation state of +1, preferably Cu(+1), Au(+1), or Ag(+1). X is a counter-ion. R.sub.25, R.sub.26, R.sub.27, R.sub.28, R.sub.29, R.sub.30, R.sub.31, R.sub.32 and R.sub.33 are independently hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with an adjacent. . .

SUMM In a preferred embodiment, the **metal** complexes of the invention have the formula depicted below in Structure 10: ##STR15##

SUMM In Structure 10, M is a transition **metal** ion selected from the group consisting of Cu, Ag, Au, Ni, Pd and Pt, with Au+2 being preferred. X is a counter-ion. R.sub.35, R.sub.36 and R.sub.37 are independently hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with an adjacent. . .

SUMM In a preferred embodiment, the **metal** complexes of the invention have the formula depicted below in Structure 12: ##STR17##

SUMM In Structure 12, M is a transition **metal** ion selected from the group consisting of Cu, Ag, Au, Ni, Pd and Pt. with Cu, Ni, Pd and Pt being preferred. X is a counter-ion. R.sub.38, R.sub.39, R.sub.40, R.sub.41, R.sub.42 and R.sub.43 are independently hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety. In a preferred embodiment,. . .

SUMM In a preferred embodiment, the **metal** complexes of the invention have the formula depicted below in Structure 13: ##STR18##

SUMM In Structure 13, M is a transition **metal** ion selected from the group consisting of Cu, Ag, Au, Ni, Pd and Pt, with Cu, Ni, Pd and Pt. . . preferred. E is oxygen, sulfur or selenium, with oxygen being preferred. Each X is independently a counter-ion. R.sub.44 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety. In a preferred embodiment,. . .

SUMM In one embodiment, the **metal** complexes of the present invention are labelled. By a "labelled **metal** complex" herein is meant a **metal** complex that has at least one element, isotope or chemical compound attached to enable the detection of the **metal** complex or the **metal** complex irreversible bound to a protein or enzyme, for example, in assays. In general, labels fall into three classes: a). . . labels, which may be antibodies or antigens; and c) colored or fluorescent dyes. The labels may be incorporated into the **metal** complex at any position, for example, as a substituent group. Examples of useful labels include 14C, 3H, biotin, and fluorescent. . .

SUMM The **metal** complexes of the invention are generally synthesized and purified as necessary as is known in the art and outlined in. . .

SUMM Once made, the **metal** complexes of the invention are useful in a wide variety of applications, as is generally outlined herein. In one embodiment, the **metal** complexes of the invention are useful as general bacteriostatic or bactericidal agents, antimicrobial agents and/or antiviral agents, for both topical. . .

SUMM The **metal** complexes of the invention can also be used to label proteins. Upon incubation of a **metal** complex of the invention with a protein, certain moieties on the protein will become ligands, resulting in a tightly bound protein-**metal** complex composition. The preferred ligand from a protein is the sulfur atom of the side chain of cysteine. Thus, a. . . cysteine residues either at the surface of the protein or otherwise accessible to the solvent can be labeled using the **metal** complexes of the invention.

SUMM In this embodiment, the **metal** complexes of the invention are added or contacted with the target protein. The excess **metal** complex may be separated, and the labeled protein, with the attached **metal** complex, is detected as is known in the art.

SUMM The stoichiometry of the bound **metal** complex to protein will vary depending on the number of potential ligands in or at the active site or on. . . as is understood in the art. Thus, for example, a protein which has four accessible cysteines will generally bind four **metal** complexes, etc.

SUMM Thus, the **metal** complexes of the present invention are also useful in probing the surface characteristics of a protein.

SUMM When used to bind or label proteins, the **metal** complexes can be coupled, using standard technology, to affinity chromatography columns. These columns may then be used to separate proteins from a sample. For example, depending on the specificity of the **metal** complex, proteins may be removed from a sample, or specific proteins, such as those containing cysteines at or near the. . .

SUMM In a preferred embodiment, the **metal** complexes are useful as enzyme inhibitors. The mechanism of inactivation is similar to the mechanism of protein labeling. In this embodiment, an enzyme has one or more moieties capable of binding as a ligand in the **metal** complexes of the invention. One or more of such moieties are also functionally important for enzymatic activity, and are inactivated upon contact with the **metal** complexes of the invention.

SUMM In this embodiment, a **metal** complex is contacted with the target enzyme. The sulfur atom of the cysteine side chain of an active site cysteine binds to the **metal** complex as a ligand.

SUMM . . . in the inhibition of the enzyme. The exact mechanism of the inactivation is unknown; however, several possibilities exist. The bound **metal** complex may sterically interfere with catalytic activity, i.e. it may be bound in or near the catalytic active site. Alternatively, the bound **metal** complex may interfere with the catalytic mechanism, i.e. by binding to a catalytic cysteine. Additionally, it is also possible that a functionally important moiety at the active site is reduced by the **metal** ion, and thus the enzyme is inactivated.

SUMM In a preferred embodiment, the inactivation of the enzyme by the **metal** complex inhibitor is effectively irreversible.

SUMM In an additional embodiment, metalloproteins are inactivated with the **metal** complexes of the present invention. Generally, the metals of metalloproteins have ligands such as histidine, cysteine and methionine. If one or more of these residues are inactivated using these **metal** complexes, the binding of the **metal** atom may be decreased or eliminated, thus reducing or eliminating biological

activity. Particular metalloproteins include, but are not limited to,. . . at least one cysteine to bind zinc, with the proteins that utilize two cysteines being preferred. In some cases the **metal** is bound exclusively by cysteines.

SUMM When the metalloprotein is a metalloenzyme, displacement of the active site **metal** by the **metal** complex may modulate enzyme activity. Such metalloenzymes include, but are not limited to, the carboxypeptidases, carbonic anhydrase, thermolysin, collagenase, histidinol. . .

SUMM Testing the efficacy of the **metal** complexes as inhibitors is routine, as will be appreciated in the art. When the target protein is an enzyme, testing. . .

SUMM The amount of **metal** complex inhibitor needed to inhibit a given enzyme will vary depending on the number of other reactive axial ligands on. . . enzyme with an active site cysteine and two other "surface" cysteines will generally require at least a 3:1 ratio of **metal** complex inhibitor:enzyme. The total amount bound to the enzyme may be determined as is known in the art.

SUMM Also provided are methods for inhibiting a selected protein or enzyme with the **metal** complexes of the invention. In this embodiment, the target protein is contacted or exposed to any of the **metal** complexes described herein. The **metal** complex can be targetted to a particular protein by the addition of a targeting moiety, such as a polypeptide or. . .

SUMM Also provided are methods for inhibiting a zinc finger protein, comprising contacting a zinc finger protein with a **metal** complex. By "inhibiting a zinc finger protein" herein is meant that the biological activity of the zinc finger protein is decreased or eliminated upon exposure to the **metal** complex. Generally, when the zinc finger protein is a nucleic acid binding protein, this means that the zinc finger will. . .

SUMM In some embodiments, the **metal** complex is labelled and used for example in a diagnostic assay for the detection or quantification of cysteine proteases in. . .

SUMM In the preferred embodiment, the **metal** complexes of the present invention are administered to a patient to treat cysteine protease-associated disorders. By "cysteine protease-associated disorders" or. . .

SUMM . . . implicated in diabetes, ocular disease such as glaucoma, and seizures and convulsions. Accordingly, inhibitors of carbonic anhydrase, such as the **metal** complexes of the present invention, are useful in the treatment of these conditions.

SUMM Thus, in one embodiment, the **metal** complexes are useful in the treatment of elevated intraocular pressure and glaucoma. Carbonic anhydrase has been implicated in elevated intraocular. . .

SUMM In an additional embodiment, the **metal** compounds are useful in the treatment of seizures and convulsions. Carbonic anhydrase II deficient mice have been shown to have. . .

SUMM In a further embodiment, the **metal** compounds are useful in the treatment of diabetes and abnormal renal function. Elevated levels of carbonic anhydrase have been associated. . .

SUMM In this embodiment, a therapeutically effective dose of a **metal** complex is administered to a patient. By "therapeutically effective dose" herein is meant a dose that produces the effects for. . . enzyme to be inhibited, and will be ascertainable by one skilled in the art using known techniques. In general, the **metal** complexes of

the present invention are administered at about 1 to about 1000 mg per day. As is known in. . .

SUMM The administration of the **metal** complexes of the present invention can be done in a variety of ways, including, but not limited to, orally, subcutaneously,. . . intraperitoneally, intramuscularly, intrapulmonary, vaginally, rectally, or intraocularly. In some instances, for example, in the treatment of wounds and inflammation, the **metal** complexes may be directly applied as a solution or spray.

SUMM The pharmaceutical compositions of the present invention comprise a **metal** complex in a form suitable for administration to a patient. In the preferred embodiment, the pharmaceutical compositions are in a. . .

DETD Synthesis of **metal** complexes of Structure 1

DETD A spectrophotometric assay was used to study papain enzyme activity and inhibition. Two reactions were performed (one with **metal** complex and without) using 10 .mu.M enzyme, 16 .mu.M of substrate (Ac-Tyr-Val-Ala-Asp-pNA), and 25 .mu.M of **metal** inhibitor.

DETD . . . 14 copper complex at 1 hour resulted in almost complete inhibition of papain. The reaction of the enzyme with the **metal** compounds was fast (less than 10 minutes). For every molecule of papain there was about 2.5 molecules of copper complex which suggests that a large excess of **metal** complex is not needed to inhibit the enzyme. Without being bound by theory, the putative reaction between the **metal** complex at the active site cysteine involves ligand substitution of the Cl for a Cys.

DETD . . . chromophore, p-nitroaniline was used. The reaction was carried out with 10 .mu.M thrombin, 16 .mu.M of substrate, and 1 mM **metal** inhibitor. Only about 10% of the enzyme was inhibited after incubation with the Structure 14 copper complex 1 for one. . .

DETD . . . binding assay. 25 ng of Sp1 (Promega) was incubated with 40 fmol of 34P labeled oligonucleotide with and without the **metal** complex in binding buffer (25 mM Tris, pH=8, 100 mM KCl, 2 mM DTT, 100 uM ZnCl2, and 10% glycerol). . . . copper complex showed 90% less counts, indicating loss of oligonucleotide bind. Loss of zinc finger function was observed since the **metal** complex prevented oligonucleotide binding to the zinc finger.

DETD . . . a spectrophotometric assay was used to study papain enzyme activity and inhibition. Once again, two reactions were performed (control and **metal** complex reaction) using 10 .mu.M enzyme, 16 .mu.M of substrate (Ac-Try-Val-Ala-Asp-pNA), and 25 .mu.M of Structure 15. Inhibition of papain. . .

DETD . . . a spectrophotometric assay was used to study papain enzyme activity and inhibition. Once again, two reactions were performed (control and **metal** complex reaction) using 10 .mu.M enzyme, 16 .mu.M of substrate (Ac-Try-Val-Ala-Asp-pNA), and 25 .mu.M of Structure 15. Inhibition of papain. . .

DETD Synthesis of **metal** complexes of Structure 7

DETD A spectrophotometric assay was used to study papain enzyme activity and inhibition. Once again, two reactions were performed (control and **metal** complex reaction) using 10 .mu.M enzyme, 16 .mu.M of substrate (Ac-Tyr-Val-Ala-Asp-pNA), and 25 .mu.M of Structure 24. As above, inhibition. . . spheres is dramatically different. The cysteine must bind in an axial position in this complex, since ligand substitution in the **metal** plane is not feasible.

DETD Synthesis of **metal** complexes of Structure 8

DETD Synthesis of **metal** complexes of Structure 9

DETD Synthesis of a **metal** complex of Structure 10

DETD A spectrophotometric assay was used to study papain enzyme activity and inhibition. Once again, two reactions were performed (control and **metal** complex reaction) using 10 .mu.M enzyme, 16 .mu.M of substrate (Ac-Tyr-Val-Ala-Asp-pNA), and 25 .mu.M of the Structure 28 gold complex. Inhibition of papain was observed immediately upon addition of the **metal** complex. This suggest that gold complexes can be effective inhibitors of cysteine proteases.

CLM What is claimed is:

1. A **metal** complex having the formula: ##STR34## wherein M is a transition **metal** ion selected from the group consisting of Cu, Ag, Au, Ni, Pd and Pt; A is either nitrogen or oxygen;. . . or selenium; D is carbon, boron or phosphorus; X is a counterion or a neutral coordinating ligand; R.sub.1 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or may be absent when A is oxygen, sulfur or selenium; R.sub.2 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, carbonyl oxygen, phosphonyl oxygen, or --OR.sub.5 when A is boron; R.sub.3 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, --OR.sub.5 when A is boron or phosphorus, or is absent when R.sub.2 is carbonyl oxygen; R.sub.4 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety; R.sub.5 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety; R.sub.6 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.7, may form a cycloalkyl or aryl group; R.sub.7 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.6, may form a cycloalkyl or aryl group; and R.sub.8 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or may be absent when. . .

2. A **metal** complex according to claim 1 wherein M is Cu+2.

3. A **metal** complex according to claim 1 having the formula: ##STR35## wherein E is oxygen, sulfur or selenium; R.sub.3 is hydrogen; and. . .

4. A **metal** complex according to claim 1 having the formula: ##STR36## wherein E is oxygen, sulfur, or selenium; and X is a. . .

5. A **metal** complex according to claim 1 having the formula: ##STR37## wherein E is oxygen, sulfur, or selenium; and X is a. . .

6. A **metal** complex according to claim 1 having the formula: ##STR38## wherein E is oxygen, sulfur, or selenium; and X is a. . .

7. A **metal** complex according to claim 1 having the formula: ##STR39## wherein E is nitrogen, oxygen or sulfur; and X is a. . .

8. A **metal** complex having the formula: ##STR40##

9. A **metal** complex having the formula: ##STR41## wherein M is a transition **metal** ion selected from the group consisting of Cu, Ag, Au, Ni, Pd and Pt; R.sub.4 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety; R.sub.5 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety; R.sub.6 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.7, may form a

cycloalkyl or aryl group; R.sub.7 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.6, may. . .

10. A **metal** complex having the formula: ##STR42## wherein M is a transition **metal** ion selected from the group consisting of Cu, Ag, Au, Ni, Pd and Pt; R.sub.4 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety; R.sub.5 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, or a targeting moiety; R.sub.6 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.7, may form a cycloalkyl or aryl group; R.sub.7 is hydrogen, **halogen**, alkyl, alkyl alcohol, alcohol, alkyl thiol, alkyl acid, alkyl amine, amine, aryl, a targeting moiety, or, together with R.sub.6, may. . .

11. A pharmaceutical composition comprising a **metal** complex according to claim 1, 2, 4, 5, 6, 7, 8 or 8 in admixture with a pharmaceutically acceptable carrier.

. . .

12. A method of inhibiting a cysteine protease comprising irreversibly binding a **metal** complex according to claim 1, 2, 4, 5, 6, 7, or 8 to said cysteine protease.

13. A method of treating cysteine protease associated-disorders comprising administering to a patient a therapeutically effective dose of a **metal** complex according to claim 1, 2, 4, 5, 6, 7, or 8.

IT 56-40-6, Glycine, reactions 60-18-4, Tyrosine, reactions 90-02-8, Salicylaldehyde, reactions 107-15-3, Ethylenediamine, reactions 110-72-5, N-Ethylethylenediamine 123-90-0, Thiomorpholine 156-87-6, 3-Amino-1-propanol 556-33-2 635-93-8, 5-Chlorosalicylaldehyde 1664-40-0, N-Phenylethylenediamine 17355-09-8 **46755-84-4**
(for prepn. of Group 10 and 11 transition-metal Schiff-base complexes)

L14 ANSWER 13 OF 16 USPATFULL

ACCESSION NUMBER: 96:25011 USPATFULL
TITLE: Transition **metal** olefin polymerization processes
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FILE SEGMENT: Granted
PRIMARY EXAMINER: Nagumo, Mark
LEGAL REPRESENTATIVE: Spiering, M. S., Reid, F. E.
NUMBER OF CLAIMS: 21
EXEMPLARY CLAIM: 1,16,19

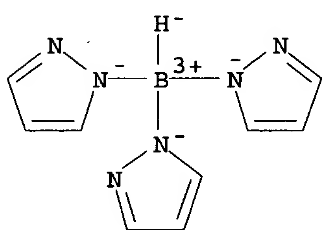
LINE COUNT: 948
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB This invention relates to processes using non-Group 4 transition **metal** compositions useful as olefin polymerization catalysts, wherein the transition **metal** is in a high oxidation state. The invention further relates to design of new ligand systems and methods of preparing and using the same. Compositions useful as catalyst precursors are neutral transition **metal** complexes comprising the unique ligand systems of the invention. The inventive compositions may be activated to a catalytic state by ion-exchange reagents or by Lewis acids.

IT **18583-60-3**, Potassium tris(pyrazolyl)borate
(reaction with vanadium oxytrichloride)

RN 18583-60-3 USPATFULL

CN Borate(1-), hydrotris(1H-pyrazolato-.kappa.N1)-, potassium, (T-4)- (9CI) (CA INDEX NAME)



● K^+

TI Transition **metal** olefin polymerization processes

AB This invention relates to processes using non-Group 4 transition **metal** compositions useful as olefin polymerization catalysts, wherein the transition **metal** is in a high oxidation state. The invention further relates to design of new ligand systems and methods of preparing and using the same. Compositions useful as catalyst precursors are neutral transition **metal** complexes comprising the unique ligand systems of the invention. The inventive compositions may be activated to a catalytic state by. . .

SUMM This invention relates to transition **metal** polymerization catalyst systems from Groups 5-10, wherein the active transition **metal** center is in a high oxidation state and stabilized by low coordination number polyanionic ancillary ligand systems, the use thereof,. . .

SUMM . . . . Ziegler-Natta type catalysts for the polymerization of olefins have been known since the 1950's. Generally, these catalysts comprise a transition **metal** halide compound, particularly one of titanium and chloride, and a **metal** alkyl cocatalyst, particularly an aluminum alkyl cocatalyst. The traditional catalyst systems are generally comprised of several chemically distinct active **metal** sites which produce different polymeric materials (molecular weight comonomer, etc.) under steady state reactor conditions. During the last 30 years. . .

SUMM . . . improve the Ziegler-Natta system has been directed towards the production of soluble, single sited olefin polymerization catalysts derived from transition **metal** precursors where the halide ligands used in tradition catalysts have been replaced by bulky, organic ancillary ligand systems, such as. . . of the catalyst center. The development of high activity catalyst systems derived from bis- and mono- Cp stabilized Group 4 **metal** precursors and alumoxanes is now well documented. Despite the fact that the cocatalyst (and therefore the resulting catalyst) is a. . .

SUMM . . . would be desirable to develop olefin polymerization catalyst comprised of later transition metals. The best studied and well defined late **metal** catalysts for the polymerization of ethylene has been developed by Brookhart and coworkers (J. Am. Chem. Soc. 1985, 107, 1443-1444).. . . containing a ligand, Cp*, a neutral datively bound ligand, L, and a reactive sigma-bound alkyl with the charge on the **metal** center balanced by a borate anion BX.sub.4-. While these catalyst systems offer some potential advantages, particularly with respect to compatibility. . . of very narrow molecular weight distributions, they suffer from very low activity and yield only a single polymer chain per **metal** atom. A goal is to develop polymerization catalysts which combine the activity and yield of cationic Group 4 systems with the selectivity and functional group tolerance of later **metal** systems.

SUMM This invention relates to Group 5-10 transition **metal** polymerization catalysts, wherein the transition **metal** is in a high oxidation state, stabilized by a low coordination number ancillary ligand system(s), the use thereof, and to methods of preparing and using the same. The catalyst is an ion-pair comprised of a coordinatively unsaturated cationic transition **metal** complex having at least one reactive **metal**-ligand sigma bond and stabilized by a low coordination number polyanionic ancillary ligand system and charge balanced by compatible non-coordinating anions. The catalyst precursor, a neutral low coordination number ancillary ligand containing transition **metal** complex, can be converted into the active ionic catalyst using Lewis acid activators such as methylalumoxane or B(C.sub.6 F.sub.5).sub.3, or. . .

SUMM The preferred catalyst of this invention are ion-pairs comprising a cationic Group 5 or 6 transition **metal** complex defined by the following formula:

SUMM M is a Group 5 or 6 transition **metal** in its highest formal oxidation state;

SUMM n is the Group number of the **metal**;

SUMM L.sub.3 and L.sub.4 are the same or different substituted or unsubstituted bulky anionic ancillary, ligands covalently bonded to the **metal**;

SUMM X is a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, **halogen**-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-substituted organometalloid radicals;

SUMM . . . preferably a single anionic coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-beating **metal** or metalloid atom, which anion is bulky, labile and capable of stabilizing the transition **metal** compound.

SUMM M is a **metal** or metalloid;

SUMM The transition **metal** component or catalyst precursor is comprised of a first component represented by:

SUMM M is a Group 5 or 6 transition **metal** in its highest oxidation state (d0);

SUMM X is independently a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, **halogen**-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-substituted organometalloid radicals;

SUMM n is the group number of the **metal**; with

SUMM . . . comprising a cation which will irreversibly react with at least one ligand, X, contained in said Group 5 or 6 **metal** compound and a compatible non-coordinating anion; with

SUMM . . . comprising a cation, which will irreversibly react with at least one ligand, X, contained in said Group 5 or 6 **metal** compound and a non-coordinating anion. Alternatively, the transition **metal** compound may be reacted with a Lewis acid capable of abstracting the ligand X to form a compatible non-coordinating anion.

DETD Key features of known single-sited olefin polymerization catalysts include a coordinatively unsaturated, electrophilic **metal** center in a trigonal environment, an active sigma bound substituent, preferably an alkyl, and at least a single vacant orbital. . . . inert ancillary ligands are present in these systems to establish and maintain the proper electronic and steric environment of the **metal** center throughout the polymerization. Ancillary ligands may be defined as ligands which do not participate in the polymerization but which are covalently bonded to the **metal** by single or multiple bonds. Ancillary ligands are typically composed of organic and/or inorganic moieties in a discrete and well. . . . olefin polymerization catalysts defined above are unstable with respect to self dimerization unless very large ancillary ligands are present. Charged **metal** complexes meeting the above defined criteria of polymerization catalysts do not require bulky ancillary ligands to prevent self-dimerization. The use. . . .

DETD The electronic nature of the **metal** centers in these systems is critical in determining the ultimate reactivity of the catalyst. For early transition **metal** systems, complexes of the highest possible formal oxidation state (d.sup.0 complexes) are preferred. In late **metal** systems such as Brookhart's cobalt complexes, the highest formal oxidation states are inaccessible. In these systems, the highest oxidation state which is accessible is desirable. Residual electron density at the **metal** center of these systems renders them more tolerant to polar functionality, but diminishes the rate of chain propagation relative to. . . . The formation of high molecular weight polymer in these systems demands a careful balancing of the electron density at the **metal** center.

DETD The challenge of capturing unique features of **metal** systems later than Group 4 lies in constructing higher oxidation state complexes which remain coordinatively unsaturated. This invention relates to. . . . charge than the number of sites they occupy. As a system, these ligands possess the unique property of oxidizing the **metal** center to a greater extent than they fill occupation sites on that **metal** and thus provide a method of maintaining high oxidation states and low coordination numbers.

DETD The single-sited olefin polymerization catalysts of this invention are comprised of a coordinatively unsaturated cationic transition **metal** complex from the Groups 5-10 of the Periodic Table (Grant

& Hackh's Chemical Dictionary. 5th ed. 1987, p. 433.) having at least one reactive **metal**--ligand sigma bond and stabilized by a low coordination number polyanionic ancillary ligand system. The ancillary ligand system is designed to stabilize the **metal** in a high oxidation state using a minimum number of coordination sites (preferably 2). Illustrative but not limiting examples of. . . system. Two ancillary ligand systems may be optionally bridged together through a bridging group, A. In addition, the cationic transition **metal** complex may be stabilized by a displaceable Lewis base ligand. The cationic transition **metal** complex is charge balanced by compatible non-coordinating anions which are weakly coordinated to the active **metal** center thereby being sufficiently labile to be displaced by a neutral Lewis base such as an olefin. As recited herein. . . bulky relative to the size of the vacant coordination site and which are resistent to chemical reactions with the active **metal** center, such as transfer of a negatively charged fragment to the cation to form neutral biproducts. Illustrative but not limiting. . .

DETD The active catalysts of this invention can be prepared from a neutral transition **metal** precursor comprising the polyanionic ligand system using a variety of activating strategies. One general strategy for forming the active catalyst. . . with an ion-exchange compound comprising a cation capable of removing a negatively charged ligand (or electron) from the neutral transition **metal** precursor and a compatible non-coordinating anion. Another approach involves the use of discrete Lewis acid coactivators such as B(C.sub.6 F.sub.5).sub.3 with the neutral transition **metal** precursor to remove an anionic non-ancillary ligand from the transition **metal** precursor to form the active catalyst cation and a non-coordinating anion comprised of the Lewis acid coordinated to the anionic. . . non-ancillary ligand. In general, active catalysts can also be generated using alumoxanes, preferrably methylalumoxane in combination with the neutral transition **metal** precursor. A more detailed description of these approaches is given below.

DETD The preferred catalysts of this invention are Group 5 and 6 transition **metal** catalysts having the following general structural features: 1) two ancillary stabilizing ligands; 2) one reactive sigma **metal**-ligand bond such as a **metal** carbon or hydride bond; 3) the **metal** center in its highest formal oxidation state (d.sup.0); and 4) a total formal charge of +1 on the transition-**metal** center. The preferred catalysts comprise the ion pair represented by the formula:

DETD M is group 5 or 6 transition **metal** in its highest oxidation state;

DETD n is the group number of the **metal**;

DETD L.sub.3 and L.sub.4 are the same or different substituted or unsubstituted anionic ancillary ligands covalently bonded to the **metal**;

DETD X is a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, **halogen**-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals;

DETD . . . . selections. Other X-ligand options are also suitable for catalysts of this invention, for example, any X-group which forms a single **metal**-ligand sigma bonds with little or no pi or multiple bond character. Thus, **metal** complexes containing **metal** X-ligands other than those listed in the formula above that are bonded to the **m tal** through a single sigma bond with no multiple bond character are operable and included in this invention.

DETD . . . . be comprised of one dianionic LCPAL, one uninegative ancillary ligand, and one uninegative ligand X, defined above. Similarly, Group 6

metal catalysts will be comprised of two dianionic LCPALs and one uninegative ligand X, or one trianionic LCPAL, one uninegative ancillary. . .

DETD . . . substituted-hydrocarbyl radical, halocarbyl radical, substituted-halocarbyl radical. hydrocarbyl-substituted organometalloid radical, halocarbyl-substituted organometalloid radical, disubstituted Group 15 radical, substituted Group 16, or **halogen** radical;
any two adjacent K groups or adjacent Rand R' groups can be joined to form a cyclic substituent; and. . .

DETD . . . precursors by alkali metals or their amalgams, reduction of neutral borole precursors within the coordination sphere of the low-valent transition **metal** complex, and deprotonation of 1-(dialkylamino)-2,5-dihydroboroles.

DETD . . . superior counter anions. Preferred non-coordinating anions comprise a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing **metal** or metalloid atom, which anion is bulky, labile and capable of stabilizing the transition **metal** cation. Anionic coordination complexes may be represented by the following formula:

DETD M is a **metal** or metalloid;

DETD The Group 5 or 6 transition **metal** catalyst described may be employed in solution, slurry, bulk-phase, high pressure or gas-phase polymerization processes, or a combination thereof, to. . .

DETD The catalysts are preferably prepared by combining at least two components, the Group 5 or 6 transition-**metal**-containing component (first component) containing at least one ligand capable of reacting with a second, ionizing activator component (second component).
The transition-**metal** component, or catalyst precursor, is comprised of the first component represented by the following formula:

DETD M is a Group 5 or 6 transition **metal** in its highest oxidation state (d.sup.0);

DETD X is independently a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, **halogen**-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-substituted organometalloid radicals;

DETD n is the group number of the **metal**;

DETD . . . comprising a cation, which will irreversibly react with at least one ligand. X, contained in said Group 5 or 6 **metal** compound and a compatible non-coordinating anion.

DETD . . . structure defined in equation 4 depends upon the choice of L.sub.3 and L.sub.4. In general, synthetic stategies for preparing transition **metal** complexes comprising the mono- and poly-valent ancillary ligands of this invention are known in the art and can be applied. . . a typical preparation the lithium salts of L.sub.3, L.sub.4, or L.sub.3 AL.sub.4 are combined in an organic solvent with the **metal** halide in its highest oxidation state. Other conventional salts such as Group 1 salts or Grignards of Group 2 salts. . .

DETD Second components useful for converting the transition **metal** precursor (4) into the catalytically active ion-pair (1) are either an ion exchange reagent as defined in equation (5) or. . .

DETD M is a **metal** or metalloid;

DETD M' is a **metal** or metalloid in its highest oxidation state;

DETD . . . portion thereof, reacts with one of the ligands of the first component, thereby generating an ion pair consisting of a transition-**metal** cation and the aforementioned anion, 'B, which anion is compatible with the transition-**metal** cation formed from the

first component. The anion must generally be capable of stabilizing the transition-**metal** cations ability to function as a catalyst and must generally be non-coordinating or sufficiently labile to permit displacement by an. . .

DETD . . . a non-reactive neutral product (X-H), a neutral Lewis base L, which may remain in solution or weakly bind to the **metal** cation, and the composition defined by equation 1. This approach is generally useful for first components having X-ligands which are. . .

DETD . . . first components of equation 4. Examples of Lewis acidic cations useful as cations of the second component include reactive transition **metal** cations such as [Cp.sub.2 MMe(NR.sub.3)].sup.+ (where M=a Group 4 **metal**), reactive carbonium ions such as [CPh.sub.3].sup.+ and tropylium, and organometallic main group cations such as [ZnMe].sup.+.

DETD . . . is B(pfp).sub.3. The neutral Lewis acid removes a negatively charged X-ligand from the first component to form the active transition **metal** cation and the compatible non-coordinating anion (e.g. when B(pfp).sub.3 is used the non-coordinating anion is B(pfp).sub.3 X.sup.-). In general, increasing. . .

DETD wherein the symbols are defined in equation 4 except there is only one X-ligand and the **metal** is in the n-1 oxidation state (d.sup.1). Examples of preferred second components for this application include [Cp'.sub.2 Fe].sup.+ ['B].sup.-, Ag.sup.+. . .

DETD Another general method involves adding one or more of the stabilizing ancillary ligands to the **metal** center subsequent to the formation of the cationic center. For example, the reaction of equimolar amounts of C.sub.2 B.sub.9 H.sub.13. . .

DETD . . . with a range of 13 to 25 are the most preferred and employed in a mole ratio of MAO to transition-**metal** component of 1:1 to 106:1.

DETD . . . the method reported by Maatta et al., (Journal of the American Chemical Society, Volume 109 (1987), pp. 7408-7416) as the **metal** component. The yield of linear polyethylene was 5.8 g.

CLM What is claimed is:

. . . olefins containing from 2 to 20 carbon atoms under polymerization conditions with a composition comprising a coordinatively unsaturated cationic transition **metal** complex having at least one reactive **metal**-ligand sigma bond, said cation stabilized by a low coordination number polyanionic ancillary ligand system and charge balanced with at least. . .

2. The process of claim 1 wherein the **metal** is one of the Groups 5 or 6 transition metals in its highest oxidation state (d.sup.0).

. . . with a composition according to the formula: ([{(L.sub.3)A(L.sub.4)}.sup.-c M.sub.n (X)].sup.+1).sub.q ['B.sup.-m].sub.p wherein: M is group 5 or 6 transition **metal** in its highest oxidation state; n is the group number of the **metal**; L.sub.3 and L.sub.4 are the same or different substituted or unsubstituted anionic ancillary ligands covalently bonded to the **metal**; X is a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, **halogen**-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals; A is an optional bridging group bridging L.sub.3 and L.sub.4 ; c is. . .

6. The process of claim 5 wherein 1 to 3 Lewis base ligands are coordinated to the **metal** cation.

. . . is a single anionic coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing **metal** or metalloid atom, which anion is bulky, labile and capable of stabilizing the transition **metal** compound.

. . . process of claim 7 wherein 'B is represented by: M[Q.sub.1 Q.sub.2 . . . Q.sub.n].sup.-d wherein: M is a **metal** or metalloid; Q.sub.1 to Q.sub.n are, independently, hydride radicals, bridged or unbridged dialkylamido radicals, alkoxide and aryloxide radicals, hydrocarbyl and. . .

. . . substituted-hydrocarbyl radical, halocarbyl radical, substituted-halocarbyl radical, hydrocarbyl-substituted organometalloid radical, halocarbyl-substituted organometalloid radical, disubstituted Group 15 radical, substituted Group 16, or **halogen** radical; any two adjacent R groups or adjacent R and R' groups can be joined to form a cyclic substituent;. . .

. . . polymerization conditions with a composition according to the formula: {(L.sub.3)A(L.sub.4)}.sup.-c M.sub.n X.sub.2 wherein: M is group 5 or 6 transition **metal** in its highest oxidation state; n is the group number of the **metal**; L.sub.3 and L.sub.4 are the same or different substituted or unsubstituted anionic ancillary ligands covalently bonded to the **metal**; X is a uninegative ligand selected from hydride radicals, hydrocarbyl radicals, **halogen**-substituted hydrocarbyl radicals, halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-substituted organometalloid radicals, halides, alkoxides, amides or phosphides; A is an optional bridging. . .

. . . The process of claim 16 wherein the composition is placed on a support, wherein when M is a Group 6 **metal** the composition comprises said A bridging group.

IT **18583-60-3**, Potassium tris(pyrazolyl)borate
(reaction with vanadium oxytrichloride)

L14 ANSWER 14 OF 16 USPATFULL

ACCESSION NUMBER: 96:21064 USPATFULL

TITLE: Process for the selective hydrogenation of epoxyalkenes to epoxyalkanes

INVENTOR(S): Puckette, Thomas A., Longview, TX, United States

PATENT ASSIGNEE(S): Eastman Chemical Company, Kingsport, TN, United States (U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 5498584		19960312	
APPLICATION INFO.:	US 1994-311628		19940923	(8)

RELATED APPLN. INFO.: Division of Ser. No. US 1994-262122, filed on 17 Jun 1994

DOCUMENT TYPE: Utility

FILE SEGMENT: Granted

PRIMARY EXAMINER: Gibson, Sharon

LEGAL REPRESENTATIVE: Thomsen, J. Frederick, Gwinnell, Harry J.

NUMBER OF CLAIMS: 7

EXEMPLARY CLAIM: 1

LINE COUNT: 757

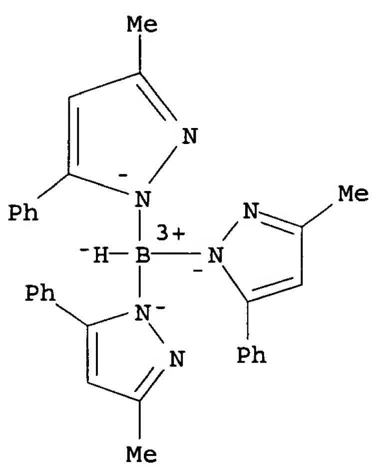
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Disclosed in a process for the homogeneous, catalytic hydrogenation of epoxyalkenes and epoxycyclo-alkenes, especially conjugated .gamma.,.delta.-epoxyalkenes and epoxycycloalkenes, to the corresponding epoxyalkanes and epoxycycloalkanes using a solution of a complex rhodium catalyst whereby the olefinic unsaturation is hydrogenated without significant hydrogenolysis of the conjugated epoxy group.

IT **162588-50-3**, Potassium tris(3-methyl-5-phenylpyrazolyl)hydridoborate
(selective hydrogenation of epoxyalkenes to epoxyalkanes using a rhodium-organophosphorus-polyunsatd. hydrocarbon catalyst)

RN 162588-50-3 USPATFULL

CN Borate(1-), hydrotris(3-methyl-5-phenyl-1H-pyrazolato-.kappa.N1)-, potassium, (T-4)- (9CI) (CA INDEX NAME)



● K^+

SUMM . . . palladium on carbon catalyst in the presence of an additive which may be a neutral salt such as an alkali **metal** halide or a base such as alkali hydroxides and amines.

SUMM . . . up to about 8 carbon atoms, a carbocyclic or heterocyclic aryl group of about 5 to 10 carbon atoms or **halogen** or any two R substituents collectively may represent an alkylene group forming a ring, e.g., alkylene containing in the main. . . (I) wherein the R substituents individually represent hydrogen, lower alkyl, e.g., alkyl of up to about 4 carbon atoms, or **halogen** or collectively represent straight or branched chain alkylene of 4 to about 8 carbon atoms, especially compounds of formula (I). . .

SUMM . . . in which at least one of the ring hetero atoms is nitrogen, e.g., pyrazolyl residues, and M is an alkali **metal** such as potassium, sodium, lithium, etc. It is apparent that those skilled in the art will recognize from the literature,. . . process of the present invention. The non-nucleophilic gegen ion may be provided as an inorganic salt such as an alkali **metal** salt or as an organic onium salt such as the salt of quaternary ammonium or phosphonium cation, e.g., tetrahydrocarbyl ammonium. . .

CLM What is claimed is:
. . . . (R.sup.5).sub.4 B.sup.- M.sup.+ wherein R.sup.5 is selected from fluorine, hydrogen, alkyl, aryl, or hetero aryl, and M is an alkali **metal**.

. . . . (R.sup.5).sub.4 B.sup.- M.sup.+ wherein R.sup.5 is selected from fluorine, hydrogen, alkyl, aryl, or hetero aryl, and M is an alkali **metal**.

IT 101-02-0, Triphenyl phosphite 111-78-4, 1,5-Cyclooctadiene 121-46-0, Norbornadiene 143-66-8, Sodium tetraphenylborate 603-35-0, Triphenylphosphine, uses 1663-45-2, 1,2-Bis(diphenylphosphino)ethane 1700-10-3, 1,3-Cyclooctadiene 2622-14-2, Tricyclohexylphosphine 3109-63-5, Tetrabutylammonium hexafluorophosphate 4731-53-7, Trioctylphosphine 4904-61-4, 1,5,9-Cyclododecatriene 7182-86-7, Tetrabutylammonium p-toluenesulfonate 7440-16-6, Rhodium, uses 7650-89-7, Tribenzylphosphine 7681-82-5, Sodium iodide (NaI), uses 7688-25-7, 1,4-Bis(diphenylphosphino)butane 10150-27-3, 1-Diphenylphosphino-2-(2-pyridyl)ethane 13755-29-8, Sodium tetrafluoroborate 14086-46-5, Dioctylphenylphosphine 14694-95-2, Tris(triphenylphosphine)rhodium chloride 14874-82-9, (Acetylacetonato)dicarbonylrhodium 14973-89-8, Tris(triphenylphosphine)rhodium bromide 14973-90-1, Tris(triphenylphosphine)rhodium iodide 15522-59-5, Tetrabutylammonium tetraphenylborate 17084-13-8, Potassium hexafluorophosphate 17185-29-4, Carbonylhydridotris(triphenylphosphine)rhodium 19845-69-3, 1,6-Bis(diphenylphosphino)hexane 62144-65-4, .alpha.,.alpha.'-Bis(diphenylphosphino)-o-xylene 111982-81-1, 2,2'-Bis(diphenylphosphinomethyl)-1,1'-biphenyl 162588-47-8, (Cyclooctadiene)bis(tribenzylphosphine)rhodium hexafluorophosphate 162588-48-9, (Cyclooctadiene)bis(tribenzylphosphine)rhodium tetrafluoroborate 162588-49-0 **162588-50-3**, Potassium tris(3-methyl-5-phenylpyrazolyl)hydridoborate
(selective hydrogenation of epoxyalkenes to epoxyalkanes using a rhodium-organophosphorus-polyunsatd. hydrocarbon catalyst)

L14 ANSWER 15 OF 16 USPATFULL
ACCESSION NUMBER: 95:16221 USPATFULL
TITLE: Process for the selective hydrogenation of epoxyalkenes to epoxyalkanes
INVENTOR(S): Puckette, Thomas A., Longview, TX, United States
PATENT ASSIGNEE(S): Eastman Chemical Company, Kingsport, TN, United States (U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 5391773		19950221	
APPLICATION INFO.:	US 1994-262122		19940617	(8)

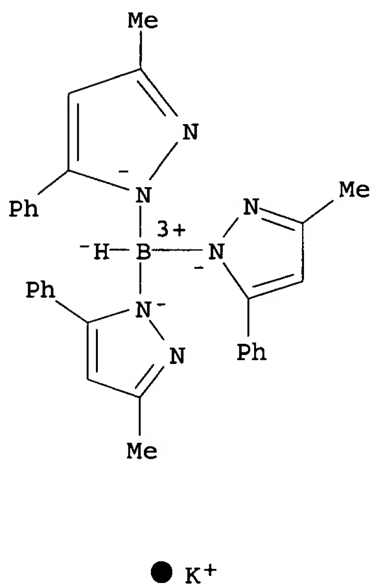
DOCUMENT TYPE: Utility
FILE SEGMENT: Granted
PRIMARY EXAMINER: Evans, Joseph E.
LEGAL REPRESENTATIVE: Thomsen, J. Frederick, Gwinnell, Harry J.
NUMBER OF CLAIMS: 7
EXEMPLARY CLAIM: 1
LINE COUNT: 751
AB Disclosed is a process for the homogeneous, catalytic hydrogenation of epoxyalkenes and epoxycycloalkenes, especially conjugated .gamma.,.delta.-epoxyalkenes and .gamma.,.delta.-epoxycycloalkenes, to the corresponding epoxyalkanes and epoxycycloalkanes using a solution of

a complex rhodium catalyst whereby the olefinic unsaturation is hydrogenated without significant hydrogenolysis of the conjugated epoxy group.

IT **162588-50-3**, Potassium tris(3-methyl-5-phenylpyrazolyl)hydridoborate
(selective hydrogenation of epoxyalkenes to epoxyalkanes using a rhodium-organophosphorus-polyunsatd. hydrocarbon catalyst)

RN 162588-50-3 USPATFULL

CN Borate(1-), hydrotris(3-methyl-5-phenyl-1H-pyrazolato-.kappa.N1)-, potassium, (T-4)- (9CI) (CA INDEX NAME)



SUMM . . . palladium on carbon catalyst in the presence of an additive which may be a neutral salt such as an alkali **metal** halide or a base such as alkali hydroxides and amines.

SUMM . . . up to about 8 carbon atoms, a carbocyclic or heterocyclic aryl group of about 5 to 10 carbon atoms or **halogen** or any two R substituents collectively may represent an alkylene group forming a ring, e.g., alkylene containing in the main. . . (I) wherein the R substituents individually represent hydrogen, lower alkyl, e.g., alkyl of up to about 4 carbon atoms, or **halogen** or collectively represent straight or branched chain alkylene of 4 to about 8 carbon atoms, especially compounds of formula (I). . .

SUMM . . . in which at least one of the ring hetero atoms is nitrogen, e.g., pyrazolyl residues, and M is an alkali **metal** such as potassium, sodium, lithium, etc. It is apparent that those skilled in the art will recognize from the literature,. . . process of the present invention. The non-nucleophilic gegen ion may be provided as an inorganic salt such as an alkali **metal** salt or as an organic onium salt such as the salt of quaternary ammonium or phosphonium cation, e.g., tetrahydrocarbyl ammonium. . .

CLM What is claimed is:
. . . an .gamma.,.delta.-epoxyalkene or an .gamma.,.delta.-epoxycycloalkene
having the formula: ##STR5## wherein each R is independently selected from hydrogen, lower alkyl, or **halogen** or collectively represent straight or branched chain alkylene of 4 to about 8 carbon

atoms.

. . . . to gram atoms of rhodium is about 2:1 to 150:1; and the R substituents individually represent hydrogen, lower alkyl, or **halogen** or collectively represent straight or branched chain alkylene of 4 to about 8 carbon atoms.

. . . . (R.sup.5).sub.4 B.sup.- M.sup.+ wherein R.sup.5 is selected from fluorine, hydrogen, alkyl, aryl, or hetero aryl, and M is an alkali **metal**.

IT 101-02-0, Triphenyl phosphite 111-78-4, 1,5-Cyclooctadiene 121-46-0, Norbornadiene 143-66-8, Sodium tetraphenylborate 603-35-0, Triphenylphosphine, uses 1663-45-2, 1,2-Bis(diphenylphosphino)ethane 1700-10-3, 1,3-Cyclooctadiene 2622-14-2, Tricyclohexylphosphine 3109-63-5, Tetrabutylammonium hexafluorophosphate 4731-53-7, Trioctylphosphine 4904-61-4, 1,5,9-Cyclododecatriene 7182-86-7, Tetrabutylammonium p-toluenesulfonate 7440-16-6, Rhodium, uses 7650-89-7, Tribenzylphosphine 7681-82-5, Sodium iodide, uses 7688-25-7, 1,4-Bis(diphenylphosphino)butane 10150-27-3, 1-Diphenylphosphino-2-(2-pyridyl)ethane 13755-29-8, Sodium tetrafluoroborate 14086-46-5, Dioctylphenylphosphine 14694-95-2, Tris(triphenylphosphine)rhodium chloride 14874-82-9, (Acetylacetonato)dicarbonylrhodium 14973-89-8, Tris(triphenylphosphine)rhodium bromide 14973-90-1, Tris(triphenylphosphine)rhodium iodide 15522-59-5, Tetrabutylammonium tetraphenylborate 17084-13-8, Potassium hexafluorophosphate 17185-29-4, Carbonylhydridotris(triphenylphosphine)rhodium 19845-69-3, 1,6-Bis(diphenylphosphino)hexane 62144-65-4, .alpha.,.alpha.'-Bis(diphenylphosphino)-o-xylene 111982-81-1, 2,2'-Bis(diphenylphosphinomethyl)-1,1'-biphenyl 162588-47-8, (Cyclooctadiene)bis(tribenzylphosphine)rhodium hexafluorophosphate 162588-48-9, (Cyclooctadiene)bis(tribenzylphosphine)rhodium tetrafluoroborate 162588-49-0 **162588-50-3**, Potassium tris(3-methyl-5-phenylpyrazolyl)hydridoborate
(selective hydrogenation of epoxyalkenes to epoxyalkanes using a rhodium-organophosphorus-polyunsatd. hydrocarbon catalyst)

L14 ANSWER 16 OF 16 USPATFULL

ACCESSION NUMBER:	93:67770 USPATFULL
TITLE:	Hydridotris(pyrazolyl)borate **metal** complexes and polymerization process
INVENTOR(S):	Newman, Thomas H., Midland, MI, United States
PATENT ASSIGNEE(S):	The Dow Chemical Company, Midland, MI, United States (U.S. corporation)

	NUMBER	KIND	DATE	
PATENT INFORMATION:	US 5237069		19930817	
APPLICATION INFO.:	US 1990-603350		19901026	(7)

DOCUMENT TYPE:	Utility
FILE SEGMENT:	Granted
PRIMARY EXAMINER:	Lee, Mary C.
ASSISTANT EXAMINER:	McKane, Joseph K.
NUMBER OF CLAIMS:	5
EXEMPLARY CLAIM:	1
LINE COUNT:	480

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

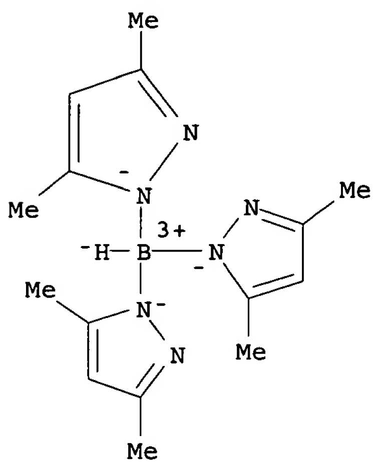
AB Hydridotris(pyrazolyl)borate complexes of Group 4 metals of the Periodic

Table of the Elements and their use in coordination polymerization processes are disclosed.

IT **17567-17-8 18583-60-3**
(reaction of, with chlorotriisopropoxytitanium)

RN 17567-17-8 USPATFULL

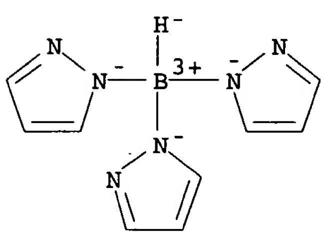
CN Borate(1-), tris(3,5-dimethyl-1H-pyrazolato-.kappa.N1)hydro-, potassium, (T-4)- (9CI) (CA INDEX NAME)



● K^+

RN 18583-60-3 USPATFULL

CN Borate(1-), hydrotris(1H-pyrazolato-.kappa.N1)-, potassium, (T-4)- (9CI) (CA INDEX NAME)



● K^+

TI Hydridotris(pyrazolyl)borate **metal** complexes and polymerization process

SUMM M is a **metal** of Group 4 of the Periodic Table of the Elements;

SUMM . . . group and are inert. The term "inert" means noninterfering with the complex's preparation or with the use of the resulting **metal** complex as a polymerization catalyst. Examples of substituted R groups include: aralkyl, alkaryl, haloalkyl, silylalkyl, haloalkyl, haloaryl,

haloalkaryl, halosilyl, haloalkarylsilyl,. . .

SUMM Hydridotris(pyrazolyl)borate complexes of metals of Group 4 of the Periodic Table of the Elements are prepared by combining an alkali **metal** hydridotris(pyrazolyl)borate compound with a halogenated Group 4 **metal** compound corresponding to the desired complex or subsequently convertible into the desired complex. Thus suitable Group 4 **metal** compounds correspond to the formula:

SUMM . . . as inertly substituted monovalent pyrazol derivatives. Examples include C.sub.1-6 alkyl pyrazolyl derivatives such as 3,5-dimethylpyrazolyl, trimethylpyrazolyl, etc. A preferred alkali **metal** hydridotris(pyrazolyl)borate compound is potassium hydridotris(pyrazolyl)borate. The procedure for preparing the complexes of the invention is analogous to that described in. . .

SUMM . . . according to any known technique. One such technique includes the reaction of a trialkylaluminum, such as trimethylaluminum, and a hydrated **metal** salt as disclosed by Kaminsky in U.S. Pat. No. 4,544,762, the teachings of which are herein incorporated in their entirety. . .

SUMM The hydridotris(pyrazol)borate **metal** complex and aluminum compound containing one or more Al--O, Al--N, or Al--P bonds and optional aluminum trialkyl compound are combined in a suitable diluent. In the preparation of the catalyst composition, the **metal** complex is preferably added in an inert diluent to the various aluminum compounds. The catalyst components may be suitably mixed. . . at any suitable temperature, preferably from 0.degree. C. to 100.degree. C., more suitably from 25.degree. C to 50.degree. C. The **metal** complex (I) may also be combined with the aluminum containing compounds in the presence of the monomer to be polymerized. . .

SUMM . . . prepared by combining at least two components as hereinafter disclosed. The first component is a derivative of a Group 4 **metal** containing at least one substituent which will combine with the cation of a second component (described hereinafter) or alternatively which. . .

SUMM More preferably such **metal** derivative compounds are those having organyl substituents that are either devoid of reactive hydrogens or wherein potentially reactive hydrogens are protected by bulky protecting groups. Illustrative, but not limiting examples of suitable **metal** derivative compounds include:
[hydridotris(pyrazolyl)borate]tribenzylzirconium,
[hydridotris(pyrazolyl)borate]tribenzyltitanium,
[hydridotris(pyrazolyl)borate]trimethyltitanium,
[hydridotris(pyrazolyl)borate]trimethylzirconium,
[hydridotris(pyrazolyl)borate]trineopentyltitanium,
[hydridotris(pyrazolyl)borate]triphenylzirconium,
[hydridotris(pyrazolyl)borate]trineopentylzirconium,
[hydridotris(pyrazolyl)borate]di(m-tolyl)titanium,
[hydridotris(pyrazolyl)borate]di(p-tolyl)zirconium,
[hydridotris(pyrazolyl)borate]trimethyltitanium hydride,
[hydridotris(pyrazolyl)borate]tri(diphenylmethyl)zirconium,
hydridotris(pyrazolyl)borate]diphenylmethylzirconium,
[hydridotris(pyrazolylborate)]dimethyl-(isopropoxy)-titanium,
[hydridotris(pyrazolyl]borate)di(isopropoxy)-titanium,
[hydridotris(pyrazolylborate)]dibenzyl(phenoxy)zirconium,
[hydridotris(pyrazolyl)borate]dibenzyl(isopropoxy)zirconium,. . .

SUMM . . . an oxidizing cation and a compatible, noncoordinating anion. Preferred anions are those containing a single coordination complex comprising a charge-bearing **metal** or metalloid core which

anion is relatively large (bulky), capable of stabilizing the active Group 4 cation formed when the. . .

SUMM . . . are not limited to, boron, phosphorus, silicon and the like. Compounds containing anions which comprise coordination complexes containing a single **metal** or metalloid atom are, of course, well known. In light of this, salts containing anions comprising a coordination complex containing. . .

SUMM . . . is a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing **metal** or metalloid atom, which anion is bulky and stable under the oxidation and subsequent polymerization conditions, and which anion is. . .

SUMM M' is a **metal** or metalloid selected from Groups 5-15 of the Periodic Table of the Elements;

SUMM Suitable oxidizing cations include organic and inorganic cations having sufficient electronegativity to oxidize the **metal** derivatives. Organic oxidizing cations for use in the compounds corresponding to formula (IV) include ferrocenium ions, indenium ions and cationic. . .

SUMM . . . bound by any particular theory of operation it is believed that the oxidizing cation causes the molecular oxidation of the **metal** derivative, and in the process becomes a neutral species. The oxidized **metal** derivative loses a hydrogen or hydrocarbyl radical by a unimolecular elimination reaction. Two or more such radicals form a hydrogen. . .

SUMM . . . from 1 to 10, more suitably from 1 to 6, most suitably from 1 to 4, carbon atoms: or a **halogen** atom. Preferably such monomers include: styrene, chlorostyrene, n-butyl styrene, etc., with styrene being especially suitable.

CLM What is claimed is:

. . . corresponding to the formula: HY.multidot.M.multidot.X'.sub.n .multidot.X.sub.3 or [HY.multidot.M'.sub.n .multidot.X.sub.2].sup.+ A.sup.- wherein: HY is a hydridotris(pyrazolyl)borate ion, M is a **metal** of Group 4 of the Periodic Table of the Elements X each occurrence is an inert anionic ligand selected from. . .

IT **17567-17-8 18583-60-3**
(reaction of, with chlorotriisopropoxytitanium)

=> log y

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	116.11	396.88

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE ENTRY	TOTAL SESSION
CA SUBSCRIBER PRICE	-2.48	-2.48

STN INTERNATIONAL LOGOFF AT 10:33:29 ON 20 JUN 2002